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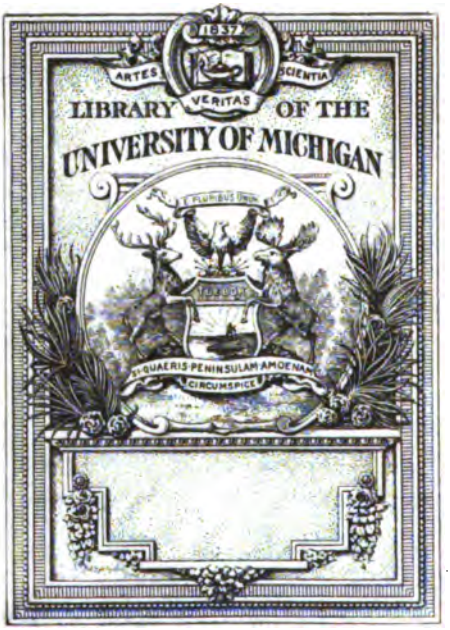
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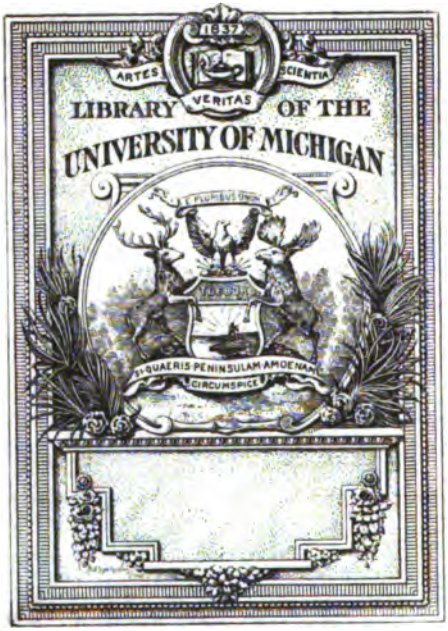
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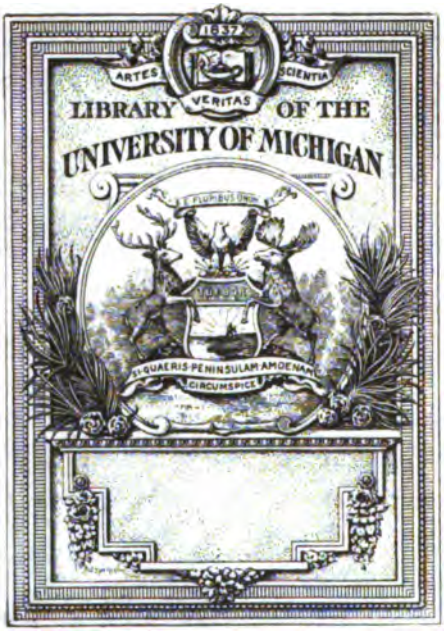
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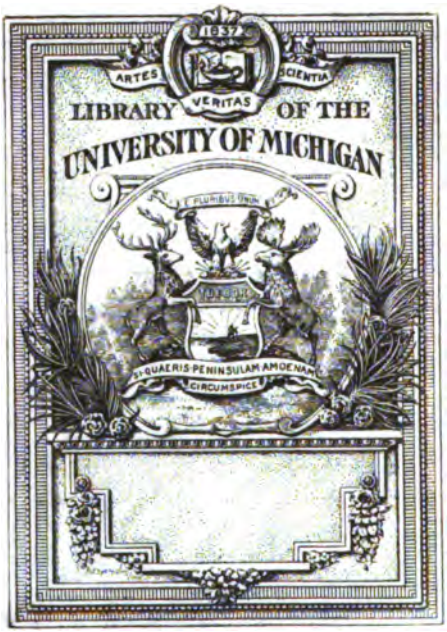
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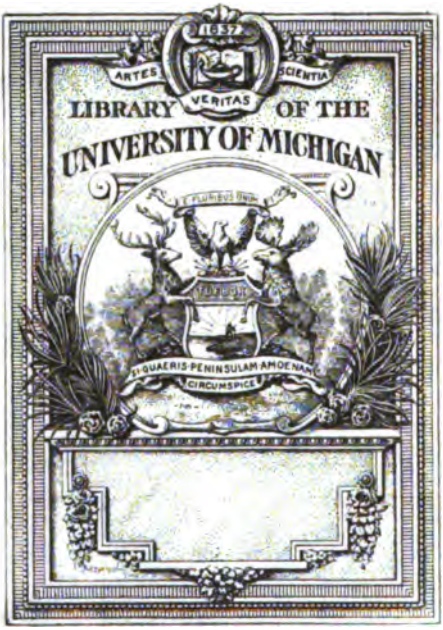
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THE CHEMISTRY OF CYANOGEN COMPOUNDS

AND THEIR MANUFACTURE AND ESTIMATION

BY

HERBERT E. WILLIAMS

PHILADELPHIA
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PREFACE

SOME years ago the author was interested in the production of cyanogen compounds, but found no up-to-date work on the subject : the information with regard to these bodies in the existing chemical dictionaries was unsatisfactory and often incorrect and misleading.

There were several excellent books dealing with the production and application of cyanides, but such chemistry as these books contained was mainly copied from the existing dictionaries and was characterised by the same inaccuracy and unsatisfactory nature.

The chemistry of these compounds had, however, not been left unregarded, as some considerable amount of original research and information has been published in the numerous technical and scientific journals, most of which is swamped by the great tide of organic chemistry of the last quarter of a century.

An attempt has been made by the author covering a number of busy years, to check the composition and properties of the cyanogen compounds, particularly the metallic salts, but although many hundreds of these compounds have been prepared and examined, the task has so far proved too great to complete, and the major portion yet remains to be accomplished.

In this little book an effort has been made to rescue

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the information scattered through the scientific press—a task of no mean magnitude, as the index of many of the journals was of little if any use—to check the composition and properties of the compounds described as far as possible ; and to add a small quota to our knowledge of these compounds by such reactions as were brought to light in the course of the author's work. An attempt was made to publish some of the information so obtained through the scientific societies, but it was found that the time required to comply with the petty restrictions and to conform to the stereotyped methods—usually quite irrelevant to the subject-matter—was so great that it was much better employed in further investigation.

The book has been arranged to give an outline of the compositions and properties of the various cyanogen compounds ; and to describe briefly the manufacture, application and estimation of such compounds as are met with in commerce.

Great care has been taken to record the various sources from which the information has been taken, and it is hoped that all such sources are duly acknowledged.

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ABBREVIATIONS OF THE TITLES OF JOURNALS, ETC.

Abbreviated title	*Journals, etc.*
A.	= Liebig's Annalen der Chemie
Am. Chem. J.	= American Chemical Journal
Ann. Chim. Anal.	= Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie, et à la Biologie
Ann. Chim. Phys.	= Annales de Chimie et de Physique
Ann. Sci. Univ. Jassy	= Annales scientifiques de l'Université de Jassy
Arch. Pharm.	= Archiv. der Pharmazie
Atti R. Accad. Lincei	= Atti della Reale Accademia dei Lincei
Ber.	= Berichte der deutschen chemischen Gesellschaft
Boll. chim. farm.	= Bollettino chimico farmaceutico
Bull. Soc. chim.	= Bulletin de la Societé chimique de France
Chem. News	= Chemical News
Chem. World	= Chemical World
Chem. Zeit.	= Chemiker Zeitung
Chem. Zentr.	= Chemisches Zentralblatt
Compt. rend.	= J Comptes rendus hebdomadaires des Séances de l'Academie des Sciences
D.P.J.	= Dingles polytechnisches Journal
E.P.	= English Patent
Gazz.	= Gazzetta chimica italiana
J.	= Jahresbericht über die Fortschritte der Chemie und verwandter Theile
J. Am. Chem. Soc.	= Journal of the American Chemical Society
J.C.M.M.S.,S.A.	= Journal of the Chemical Metallurgical and Mining Society of South Africa
J.C.S.	= Journal of the Chemical Society
J. Ind. Eng. Chem.	= Journal of Industrial and Engineering Chemistry
J. Pharm. Chim.	= Journal de Pharmacie et de Chimie
J. pr. Chem.	= Journal für praktische Chemie
J. Russ. Phys. Chem. Soc.	= Journal of the Physical and Chemical Society of Russia
J.S.C.I.	= Journal of the Society of Chemical Industry

Abbreviated title	*Journals, etc.*
J. S. Dy. & Col.	= Journal of the Society of Dyers and Colourists
P.	= Proggendorff's Annalen der Physik und Chemie
P.C.S.	= Proceedings of the Chemical Society
Pharm. Weekblad	= Pharmaceutisch Weekblad
Phil. Trans.	= Philosophical Transactions of the Royal Society of London
R.P.	= Repertorium für die Pharmacie
T.C.S.	= Transactions of the Chemical Society
U.S.A. Pt.	= United States of America Patent
Z. anal. chem.	= Zeitschrift für analytische Chemie
Z. angew. chem.	= Zeitschrift für angewandte Chemie
Z. anorg. chem.	= Zeitschrift für anorganische Chemie
Z. Kryst Min.	= Zeitschrift für Krystallographie und Mineralogie
Z. öffentl. Chem.	= Zeitschrift für öffentliche Chemie

THE CHEMISTRY OF CYANOGEN COMPOUNDS

PART I

CHAPTER I

CYANOGEN AND THE CYANOGEN HALOIDS

As hydrocyanic acid (prussic acid) may be produced by the fermentation of certain glucosides, which occur naturally in a few plants, it is possible that hydrocyanic acid was used by the ancients as a poison. The first authentic knowledge of the compounds of cyanogen, however, date from the discovery of prussian blue in 1704 by Diesbach; but little was known of the chemical properties of the compound until Maequer in 1754 prepared potassium ferrocyanide by crystallizing the filtered solution, obtained by treating the blue with caustic potash.

The discoveries of Scheele in 1782–83, Berthollet in 1790, and Gay Lussac in 1815, considerably advanced the knowledge of the chemistry of prussian blue and potassium ferrocyanide, and clearly showed the relation of these bodies to hydrocyanic acid and cyanogen; the brilliant work of Liebig and Wöhler in this field very considerably increased our knowledge of this interesting series of compounds, a knowledge that has steadily increased from that time to the present day.

Although hydrocyanic acid had been prepared by Scheele in 1782, it was not until 1815 that cyanogen

was isolated in a pure state by Gay Lussac. The discovery of this gas was one of far-reaching importance to theoretical chemistry, as it is the first recorded instance of the isolation of a compound radicle.

Cyanogen may be fairly readily obtained by a number of reactions, such as :

1. The action of heat on the cyanides of the noble metals :

$$Hg(CN)_2 = Hg + (CN)_2.$$

2. By the dry distillation of ammonium oxalate in the presence of a dehydrating substance, such as phosphorous pentoxide :

$$(NH_4)_2C_2O_4 + 2P_2O_5 = (CN)_2 + 2H_4P_2O_7 ;$$

or with glycerine :

$$(NH_4)_2C_2O_4 = (CN)_2 + 4H_2O.$$

3. By heating dry potassium ferrocyanide with mercuric chloride :

$$K_4Fe(CN)_6 + 3HgCl_2 = 4KCl + FeCl_2 + 3Hg + 3(CN)_2.$$

4. By heating dry zinc cyanide and cupric chloride to 160°–170° C. :

$$2Zn(CN)_2 + 2CuCl_2 = 2Cu(CN) + (CN)_2 + 2ZnCl_2.$$

5. It may also be prepared in the wet way, by boiling a solution of cupric sulphate, or chloride, to which is gradually added through a stoppered funnel a strong solution of sodium, or potassium cyanide.[1] The cupric cyanide at first formed decomposes into cuprous cyanide and cyanogen :

$$4KCN + 2CuSO_4 = 2CuCN + (CN)_2 + 2K_2SO_4.$$

The cyanogen is evolved in abundance together with water vapour ; no reaction occurs with the latter, and the cyanogen at the temperature of the reaction, nor is any of the evolved cyanogen converted into para-cyanogen.

6. The gas may also be produced in a manner similar to the preparation of chlorine ; thus when

[1] Jacquemin, *Compt. rend.* (1885), **100**, 1005.

sodium, or potassium cyanide solution is electrolyzed, using an iron cathode and a carbon anode, cyanogen gas is liberated at one pole and hydrogen at the other. It may also be produced by distilling a cyanide with manganese dioxide and sulphuric acid.

Dry cyanogen gas is most conveniently prepared by the dry distillation of mercuric cyanide (Gay Lussac); or any dry cyanide, or ferrocyanide mixed with the equivalent quantity of mercuric chloride, the gas being collected over metallic mercury. A portion of the cyanogen, however, polymerizes to form a dark brown substance called paracyanogen. It is necessary that the cyanide used should be quite dry, otherwise the water-vapour will react with the cyanogen at the temperature of the tube to form ammonia, carbon dioxide, and hydrocyanic acid :

$$(CN)_2 + 2H_2O = HCN + NH_3 + CO_2.$$

Cyanogen gas is colourless and inflammable, burning with a peach-coloured flame ; it has a pungent odour, but strongly suggests hydrocyanic acid ; it attacks the eyes and nose, and is excessively poisonous. Under a pressure of about 4 atmospheres at normal temperature, or at normal pressure but cooled to − 20.7° C., cyanogen gas is condensed to a transparent, colourless, and very mobile liquid of sp. gr. 0.866 at 17° C., and on further cooling may be obtained in crystals melting at − 34.4° C. It has a critical temperature of 128.3° C. and a critical pressure of 5 or 6 atmospheres.[1]

It is decomposed into its elements by the electric spark, and does not readily unite directly with hydrogen, only a trace of hydrocyanic acid being formed by passing the two gases through a tube heated to 500° C. ; combination, however, takes place when the mixed gases are heated to 500° C. in a sealed tube.

Water dissolves four and a half times its own volume of the gas ; alcohol twenty-five times and

[1] E. Cardoso and G. Baumé, *Compt. rend.* (1910), **151**, 141–43 ; *J.C.S.*, i. 605 (1910).

ether five times. The aqueous solution rapidly becomes dark coloured with formation of azulmic acid, ammonium oxalate and carbonate, hydrocyanic acid, urea, and other products.

Metallic sodium or potassium combine directly with cyanogen when heated in the gas, to form a cyanide of the alkali metal.

The gas when passed into a solution of an alkali hydroxide forms a mixture of cyanide and cyanate :

$$2KOH + (CN)_2 = KCN + KCNO + H_2O.$$

By substituting a solution of a sulphide for the hydroxide a mixture of cyanide and thiocyanate is formed :

$$K_2S + (CN)_2 = KCN + KCNS.$$

When passed into strong aqueous hydrochloric acid, crystals of oxamide, $C_2N_2H_4O_2$, are deposited after some time, while a small quantity of ammonium oxalate remains in solution. Strong aqueous hydriodic acid also yields oxamide, with liberation of iodine ; and the solution contains hydrocyanic acid and ammonium iodide.

By the action of nascent hydrogen, cyanogen is converted into ethylene diamine :

$$(CN)_2 + 4H_2 = (C_2H_4)N_2H_4 ;$$

and it combines directly with hydrogen sulphide to form a mono- and di-cyanogen sulphydrate.

Glacial acetic acid absorbs about eighty times its own volume of cyanogen, and it is also absorbed by a 3 per cent. solution of hydrogen peroxide with evolution of oxygen ; if a little caustic potash solution is added after a few minutes, needles of oxamide separate free from by-products.[1]

The gas also combines directly with certain organic bases, such as aniline, toluidine, etc., and this reaction has been recommended for the removal of cyanogen from mixed gases ; but, as has been pointed out by

[1] B. Radziszewski, *Ber.* **23**, 355.

M. Loeb,[1] both carbon monoxide and dioxide would react, decomposing the compound.

By passing cyanogen into a 40 per cent. aqueous solution of azoimide, cyanotetrazol (tetrazole – 5 – carbonylonitrile), C_2HN_5, is produced.[2] The product melts at 99°, forming a reddish-brown liquid, and yields ammonia quantitatively when boiled with caustic potash solution; the silver salt, AgC_2N_5, and the barium salt $Ba(C_2N_5)_2 3\frac{1}{2}H_2O$, have been prepared.

As cyanogen may be obtained by heating oxamide with phosphorous pentoxide, it has been considered as the nitrile of oxalic acid with the formula :

$$N \equiv C - C \equiv N.$$

According to Dixon and Taylor,[3] the formula should be :

$$\begin{matrix} C = C \\ \| \quad \| \\ N — N \end{matrix}$$

PARACYANOGEN, $(CN)_x$. When the dry cyanide of a noble metal, such as the silver, or mercury salt is ignited, cyanogen is evolved with liberation of the metal; part of the cyanogen, however, at the temperature necessary for the reaction, polymerizes to form a dark brown substance called paracyanogen : a larger yield of the compound is obtained when the silver cyanide is ignited than when the mercury salt is used. It is also obtained when cyanogen gas is heated under pressure in a closed vessel, the amount formed varying with the temperature and pressure; but high pressure, although favouring the formation of paracyanogen, also tends to decompose the cyanogen into its elements.

Paracyanogen is a dark, brownish-black compound, insoluble in water or alcohol, but soluble in concentrated sulphuric acid in the cold, from which it may be precipitated unchanged by dilution with

[1] *J.C.S.*, liii. 812.

[2] E. Oliveri-Mandola and T. Passalaeque, *Gazetta* (1911), 41, ii. 430; *J.C.S.* (1912), i. 144.

[3] *T.C.S.* (1913), 982.

water. It may be reconverted into normal cyanogen gas by heating to about 860° C. in a current of inert gas, such as nitrogen or carbon dioxide; heated in a current of hydrogen, it is converted into hydrocyanic acid, ammonia, and carbon.

CYANOGEN HALOIDS

CYANOGEN BROMIDE, CNBr. 1. This body was discovered by Serullas in 1827,[1] and is easily produced by the action of bromine on an aqueous solution of hydrocyanic acid or a soluble cyanide:

$$HCN + Br_2 = HBr + CNBr;$$
$$\text{or } NaCN + Br_2 = NaBr + CNBr.$$

2. It may also be produced by the electrolysis of a solution of sodium bromide and cyanide.

3. By heating a mixture of sodium cyanide, sodium bromide and manganese dioxide with sulphuric acid:[2]

$$NaBr + NaCN + MnO_2 + 2H_2SO_4 =$$
$$CNBr + Na_2SO_4 + MnSO_4 + 2H_2O.$$

4. And by heating a mixture of sodium thiocyanate and sodium bromide with an oxidizing agent:

$$NaBr + NaCNS + 2O_2 = Na_2SO_4 + CNBr.$$

A mixture of the two salts is run into the oxidizing agent kept at 100° C., which may, for example, be a solution of a mixture of nitric and sulphuric acid, but containing 20 per cent. of nitric acid.

The most convenient mode of preparing the compound is to add the bromine to a cooled solution of potassium cyanide; when the reaction is complete the mixture is gently warmed, and the sublimed bromide condensed in a receiver surrounded by freezing mixture. This process has been slightly modified by R. Scholl,[3] who recommends the following proportions, whereby a 90 per cent. yield is obtained; a solution of 65 grams of potassium cyanide in 120 c.c. of water are cooled

[1] *Ann de Phys.* (2), **34**, 100, **35**, 294.
[2] *E.P.*, 2660 (6.2.95). [3] *Ber.* (1896), **29**, 1822–25.

to 0° C., and slowly added to 150 grm. of bromine also cooled to 0° C., and the liquid agitated while mixing; the product is then distilled at 60° to 70° C., and the evolved cyanogen bromide condensed.

Cyanogen bromide is thus obtained in long, delicate prisms which slowly change to cubes; it is very volatile, and its vapour, which has a pungent odour, attacks the eyes and nose, causing tears; it is exceedingly poisonous, and its vapour dangerous to inhale, one grain of the solid being sufficient to kill a rabbit instantly. The compound is very soluble in water and alcohol, and it also dissolves in cold strong sulphuric, nitric, or hydrochloric acid without decomposition, and combines with ammonia, forming a mixture of ammonium bromide and cyanamide:

$$CNBr + 2NH_3 = NH_4Br + H_2CN_2.$$

With aqueous sulphurous acid decomposition occurs with formation of sulphuric, hydrobromic, and hydrocyanic acids:

$$H_2SO_3 + CNBr + H_2O = H_2SO_4 + HCN + HBr.$$

Aqueous caustic alkalis convert it into a cyanide, bromide, and a bromate:

$$3CNBr + 6KOH = 3KCN + 2KBr + KBrO_3 + 3H_2O.$$

Cyanogen bromide melts at 52° C. and boils at 61° C.

Antimony heated in its vapour yields antimony bromide and cyanogen; while metallic mercury decomposes the aqueous solution in a similar manner, with production of mercuric bromide and cyanogen.

When treated with hydrogen sulphide, hydrothiocyanic, and hydrobromic acids are formed:

$$CNBr + H_2S = HCNS + HBr.$$

But if the reaction takes place in the presence of hydrochloric acid, hydrocyanic and hydrobromic acids are formed together with free sulphur:[1]

$$CNBr + H_2S = HCN + HBr + S.$$

[1] A. E. Dixon and Taylor, *P.C.S.* (1913), 90.

With alkaline sulphides the corresponding bromide and thiocyanate are formed.[1]

When cyanogen bromide is treated with thiocarbamide and sodium bicarbonate, cyanamide together with a bromide and thiocyanate are formed, with evolution of carbon dioxide, but no cyanide. The reaction may be expressed thus :

$$CNBr + CSN_2H_4 = HBr + HCNS + H_2CN_2$$

The reaction proceeds differently in the presence of strong acids, hydrocyanic and hydrobromic acids being formed and a salt of formamidine disulphide ; but in neutral solutions both of these reactions take place.[2]

Cyanogen bromide is slowly decomposed by water.

Cyanogen bromide is sometimes used in conjunction with a dilute cyanide solution in the process of Sulman and Teed for the treatment of refractory gold ores, such as the telluride gold ores of Western Australia. For this purpose it is usually made on the spot owing to the extreme difficulty of transporting the material.

From a study of the reactions of these compounds, Gutmann [3] has suggested the structural formula :

where X = chlorine, bromine or iodine.

POLYMERIC CYANOGEN BROMIDE, or **CYANURIC BROMIDE,** $(CN)_3Br_3$, is known, and may be prepared in good yield by the action of moist hydrobromic acid on a solution of cyanogen bromide in benzene. It combines with 10 per cent. hydrazine to form cyanuric trihydrazide ; with an ethereal solution of phenylhydrazine, cyanuric triphenylhydrazide is formed ; and with carbamide it unites at 130° – 140° C. to form tricarbamylmelamine.[4]

[1] Gutmann, *Ber.* (1909), **42**, 3628.
[2] A. E. Dixon and Taylor, *T.C.S.* (1913), 980.
[3] *Ber.*, **42**, 3623.
[4] E. von Meyer, *J. pr. Chem.* (1910) [ii], **82**, 321–38.

CYANOGEN CHLORIDE, CNCl, was discovered by Berthollet [1] and investigated by Gay Lussac [2] and others, who demonstrated its true nature and properties.

It is prepared by passing chlorine into aqueous hydrocyanic acid, or by allowing chlorine to act on moist mercuric cyanide in the dark.

The gas was prepared by Gay Lussac, by passing chlorine into an aqueous solution of hydrocyanic acid, but is more generally prepared by leaving moist mercuric cyanide in contact with chlorine in a large flask in the dark, and at the ordinary temperature, the excess of chlorine being removed by agitation with metallic mercury, and the gas dried by passing over fused calcium chloride.

It may also be prepared by the action of hydrochloric acid on a mixture of bleaching powder and an alkaline cyanide; [3] and in a similar manner to the preparation of the bromide, by the action of oxidizing agents on a mixture of an alkali metal chloride and thiocyanate; [4] or by electrolysis of a mixture of sodium cyanide and chloride.[5]

Cyanogen chloride is a gas with a powerful odour; it attacks the eyes and is excessively poisonous and the greatest care should be taken in its preparation. It has a specific gravity of 2·12, and when cooled to below — 6° C. it solidifies in long transparent prisms. It is soluble in water, alcohol, and ether; at 20° C. water dissolves twenty-five times its volume of the gas, alcohol about one hundred times its own volume, and ether about fifty times its volume.

When kept in sealed tubes for some time the gas gradually polymerizes to solid cyanuric chloride, and when treated with alkalis it is converted into a chloride and a cyanate. Antimony heated in the gas yields antimony chloride and free cyanogen; the gas also

[1] *Ann. Chem.*, 1, 35.
[2] *Ann. Chem.*, 90, 200.
[3] E. Morgan, E.P., 2660 (6.2.95).
[4] E.P., 9710 (26.5.00).
[5] E.P., 2660 (6.2.95).

combines with certain anhydrous chlorides to form compounds such as

$$Sb_2Cl_5CNCl\ ;\ BCl_3CNCl\ ;\ FeCl_3CNCl,\ \text{etc.}$$

Treated with an alkali sulphide, a thiocyanate and chloride are formed.[1] With sodium sulphite, the cyanide, chloride, and sulphate of sodium are formed.[2]

Solid cyanogen chloride or cyanuric chloride, $(CN)_3Cl_3$, is a polymeric modification of cyanogen chloride, and was first discovered by Serullas in 1827,[3] who considered it to be cyanogen bichloride, but its true composition was afterwards demonstrated by Liebig.

Cyanuric chloride is formed when gaseous cyanogen chloride is kept for some time, the polymeric change being considerably hastened by sunlight ; it was prepared by Liebig, by heating potassium thiocyanate in chlorine gas :

$$3KCNS + 6Cl_2 = 3KCl + (CN)_3Cl_3 + 3SCl_2.$$

It may also be prepared by the action of phosphorous pentachloride on dry cyanuric acid :

$$H_3C_3N_3O_3 + 3P_2Cl_5 = (CN)_3(Cl)_3 + 3P_2OCl_3 + 3HCl.$$

Cyanuric chloride is obtained in monoclinic needles, which melt at 140° C. to a colourless liquid and on further heating boils at 190° C. ; the vapour has an odour suggesting chlorine, and like the other cyanogen haloids it is exceedingly poisonous, and attacks the eyes, causing tears.

The compound is slightly soluble in water. The solution decomposes slowly in the cold with formation of hydrochloric and cyanuric acids :

$$(CN)_3Cl_3 + 3H_2O = (CN)_3(OH)_3 + 3HCl.$$

The rate of decomposition increases as the temperature rises : it dissolves readily in alcohol and ether.

CYANOGEN IODIDE was discovered by Sir Humphry Davy in 1816.[4] It cannot be prepared by the

[1] Gutmann, *Ber.*, **42**, 3623.
[2] Gutmann, *l.c.*
[3] *Ann. Ch. Phys.* [2], **35**, 291, 337.
[4] H. Davy, *Gilb. Ann.*, 54, 384.

direct union of cyanogen and iodine, but may be obtained, by the action of the iodine on an aqueous solution of a cyanide ; the iodine is added to a strong aqueous solution of potassium cyanide, the mixture is then gently warmed and the sublimed cyanogen iodide condensed in a cooled receiver. The action of iodine on aqueous hydrocyanic acid only results in the conversion of a portion of the cyanogen into the iodide, the reaction :

$$HCN + I_2 \rightleftarrows CNI + HI$$

being a reversible one, a larger proportion is obtained by dilution or by increasing the temperature.

It is best prepared by thoroughly mixing one part of iodine with two parts of silver cyanide in a retort which is then gently heated, and the vapours conducted into a cooled receiver, where it crystallizes in white crystals. Mercuric cyanide may be substituted for the silver salt, but the resulting cyanogen iodide should be purified by resublimation on the water-bath.

Cyanogen iodide may also be prepared by most of the general methods described under cyanogen bromide and chloride, by which it is usually obtained with greater ease and in better yields.

Cyanogen iodide crystallizes in fine long white needles and is exceedingly poisonous. Like the other cyanogen haloids it attacks the eyes and nose. The solid compound slowly volatilizes at the ordinary temperature, and it is only sparingly soluble in water, but dissolves more readily in alcohol, and in ether : it is also soluble in many volatile and fixed oils.

It is unacted upon by nitric, or cold hydrochloric acids ; but is completely decomposed by hot strong sulphuric acid, and it is also decomposed by the action of hydriodic or sulphurous acids, hydrogen sulphide, stannous chloride, and reducing agents generally, but it is very stable towards oxidizing agents ; it is also decomposed by caustic alkalis, and with formation of cyanogen and mercuric iodide by agitating the aqueous solution with metallic mercury.

With a solution of potassinm sulphide it is completely converted into potassium thiocyanate and iodide : [1]

$$K_2S + CNI = KCNS + KI.$$

With aqueous sodium hydroxide, and arsenious acid in presence of carbon dioxide, sodium cyanide, iodide, and arsenate are formed.[2]

CYANOGEN SULPHIDES. Cyanogen gas does not unite directly with sulphur or with dry hydrogen sulphide, but if the latter gas is moist and mixed with an excess of cyanogen, yellow needles are formed of cyanogen monosulphide, $(CN)_2H_2S$; this compound is soluble in water, alcohol, and ether, but the aqueous solution decomposes on keeping. When heated with dilute alkalis, or acids, it is converted into ammonia, oxalic acid, and hydrogen sulphide :

$$(CN)_2H_2S + 4H_2O = (NH_4)_2C_2O_4 + H_2S;$$

but with strong aqueous caustic alkalis the decomposition proceeds differently, a cyanide and a thiocyanate being formed :

$$(CN)_2H_2S + 2KOH = KCN + KCNS + 2H_2O.$$

If cyanogen gas is mixed with an excess of hydrogen sulphide and the mixed gases passed into water or alcohol, yellowish red crystals separate out of the liquid, of cyanogen disulphide, $(CN)_22H_2S$; this compound is slightly soluble in water, and in alcohol, and ether ; it dissolves without decomposition in cold dilute caustic potash, but is decomposed by boiling into potassium sulphide, oxalate and ammonia ; with strong caustic solution it yields a cyanide and a thiocyanate.

By the action of silver thiocyanate on an ethereal solution of cyanogen iodide, a compound is formed which may be considered as cyanogen sulphide, the product may be purified by sublimation, or by solution in boiling carbon disulphide. It may also be produced by the action of sulphur chloride on silver, or mercuric

[1] Gutmann, *Ber.*, **42**, 3623–31. [2] Gutmann, *l.c.*

cyanide ; or by the reaction of cyanogen iodide and silver sulphide.

The compound sublimes between 30° to 40° C., and melts at 60° C. ; it dissolves in ether, and water, and is readily decomposed by dilute sulphuric, hydrochloric, or nitric acids ; and by the action of nascent hydrogen, hydrogen sulphide, or potassium sulphide, it forms hydrocyanic and hydrothiocyanic acids or their potassium salts.

CYANOGEN SELENIDE. When chlorine or nitrogen dioxide is allowed to act on potassium selenocyanide, cyanogen triselenide is formed, but with small yield, most of the selenium being oxidized to selenious or selenic acids. According to W. Mulhmann and E. Schröder [1] the following method yields much better results.

Potassium selenocyanide is mixed with one-third to one-half its weight of water, and spread over a flat glass basin, and nitrogen dioxide passed over it (obtained by igniting lead nitrate), the mass being stirred the whole time, and thoroughly cooled by ice.

The colour first changes to red with formation of the compound, $(CN)_2Se_4K$, and afterwards turns yellow, hydrocyanic acid and cyanogen gas being evolved. Towards the end, the action may be hastened by the addition of a little fuming nitric acid.

The product is drained on a vacuum funnel, once washed with a little distilled water, and dried over sulphuric acid ; the so dried product consists of a mixture of potassium nitrate and cyanogen triselenide, and the latter may be obtained in crystals by solution in warm pure benzene and cooling the filtered solution.

CYANOGEN TRISELENIDE is obtained in yellow plates or prismatic needles, melting at 132° C., but it decomposes at 148·5° C. with separation of selenium. It does not dissolve, but is decomposed by water, forming selenious acid and separating selenium.

It may be crystallized unchanged from fatty and aromatic hydrocarbons, chloroform, carbon tetra-

[1] *Ber.* (1900), 33 [11], 1765–69 ; *J.S.C.I.*, 19, 685.

chloride, and carbon disulphide; but is decomposed with separation of selenium by the action of nitro methane and ethyl acetoacetate.

CARBONYL CYANIDE has been described by D. Berthelot and A. Gaudechon,[1] who prepared it by exposing a mixture of carbon monoxide and cyanogen to the ultra violet light: carbonyl cyanide was obtained as a yellow amorphous compound, non-volatile at 200° C., and partly soluble in water; it dissolves in alkalis to a yellow solution, which slowly hydrolyzes on the addition of acid, giving carbon dioxide, and hydrocyanic acid.

The product could also be obtained by the silent electric discharge, but no similar product could be produced by merely heating the two gases.

OTHER CARBON AND NITROGEN COMPOUNDS

CARBON SUBNITRIDE, C_4N_2. This compound has been prepared by C. Monrew and J. C. Bongrand,[2] who obtained it by eliminating water from acetylene-dicarboxylamide:

$$NH_2 - CO \cdot C \vdots C \cdot CO \cdot NH_2 - 2H_2O = C_4N_2.$$

It may therefore be regarded as dicyanoacetylene:

$$N \equiv C - C \equiv C - C \equiv N.$$

Carbon subnitride is obtained in slender, colourless needles, which melt at 20.5° to 21° C. and boil at 76° C. (753 mm. pressure). The vapour has an odour resembling cyanogen, but is a powerful irritant, and is spontaneously inflammable at 130° C.

CARBON PERNITRIDE. When cyanogen bromide is allowed to act on a well-cooled solution of sodium azoimide in water, colourless, odourless needles of

[1] *Compt. rend.* (1913), **156**, 1766–68.
[2] *Compt. rend.* (1910), **150**, 225–27; *J.C.S.* (1910), i. 159.

carbon pernitride are formed, $N \vdots C \cdot N\langle^{N}_{N}$ or $N \vdots C.N : N \vdots N$, which are soluble in water, alcohol, ether, and benzene, but are sparingly soluble in light petroleum. The crystals melt at 35.5° to 36° C. and sublime slightly at that temperature in a vacuum, but begin to decompose at 70° C. and between 170° and 180° C. explode violently. The compound is particularly sensitive to shock, and should be prepared only in small quantities. In the presence of a trace of bromine it forms a polymeride insoluble in ether. It is gradually hydrolyzed in aqueous solutions forming azoimide and carbon dioxide.[1]

NITROGEN CARBIDES. When tetraiodoglyoxaline is heated decomposition takes place to form first the compound, C_3N_2I, and ultimately C_3N_2.[2] Similar compounds may be obtained by heating tri-iodo 5 + 2 methyl glyoxalines and tetraiodapyrrole such as C_3N_2Me and C_4NH. These three compounds are charcoal-like products, and are similar to paracyanogen in that when heated to redness in an indifferent atmosphere they yield cyanogen; when fused with alkalis the compounds dissolve forming ammonia, cyanides, and carbonates; and they readily absorb gases and moisture.

The formation of a soot-like sepia-coloured iodo-nitrogen carbide, $(C_3N_2I)_x$, takes place at 180° C., which forms a brown solution in nitric acid with liberation of iodine.

The carbide C_3N_2 is best obtained by heating tetraiodoglyoxalic acid first at 180° C. and then at 420° C. When heated to 800° to 900° C. in an atmosphere of nitrogen, cyanogen is formed quantitatively.

[1] G. Darzens, *Compt. rend.* (1912), **154**, 1232–34; *J.C.S.* (1912), i. 542.

[2] H. Pauly and E. Wattzinger, *Ber.* (1913), **46**, 3129–40; *J.C.S.* (1913), i. 1311.

CHAPTER II

CYANAMIDE AND ALLIED COMPOUNDS

NORMAL CYANAMIDE, $H_2CN_2 = N : C.NH_2$, may be prepared by the action of cyanogen bromide, chloride, or iodide, on ammonia :[1]

$$CNCl + 2NH_3 = CNNH_2 + NH_4Cl ;$$

it may also be prepared by the action of carbon dioxide on sodium amide :

$$NaNH_2 + CO_2 = NH_2COONa.$$
$$NH_2COONa = CNONa + H_2O.$$
$$CNONa + NaNH_2 = CNNNa_2 + H_2O.$$
$$\text{or } 2NaNH_2 + CO_2 = CNNNa_2 + 2H_2O.^2$$

By the action of mercuric oxide on thiourea :

$$CS(NH_2)_2 + HgO = CN_2H_2 + HgS + H_2O.^3$$

As the sodium salt as the intermediate product in the manufacture of cyanides from sodium amide :

$$2NaNH_2 + C = Na_2CN_2 + 2H_2$$

And as the calcium salt by the action of nitrogen on calcium carbide at high temperatures.

The compound may be prepared from thiourea by gradually adding freshly precipitated and well washed mercuric oxide to a cold but not saturated solution of thiourea, avoiding excess, otherwise mercuric cyanamide will be precipitated. The end of the

[1] Bineau, *A. Ch.* [2], **67**, 368 ; **70**, 251 ; Cloez a Cannzzauro, *A.*, **78**, 228.

[2] Beilstein and Geuther, *A.*, **108**, 93 ; Drechsel, *J. pr.* [2], **16**, 203.

[3] Volhard, *J. pr.* [2], **9**, 24 ; Baumann, *B*, **6**, 1371.

reaction can be determined by adding a drop of the clear liquor to a few c.c. of an ammoniacal solution of silver nitrate, the addition of mercuric oxide is continued until the test shows no black coloration. The liquid is filtered from the mercuric sulphide and concentrated as quickly as possible under a vacuum over sulphuric acid, to avoid polymerization into dicyandiamide. The cyanamide is separated from the dicyandiamide which is always formed to a certain extent by treatment with ether, in which the former is soluble, but the latter insoluble. This reaction proceeds more readily if the thiourea is impure.

Cyanamide may be prepared from the sodium salt by adding the latter to well-cooled, concentrated hydrochloric acid, distilling in a vacuum, and dissolving the cyanamide out of the residue with ether; but it may be more conveniently prepared from the commercial calcium salt, by adding a solution of aluminium sulphate to the aqueous solution of calcium cyanamide:

$$3CaCN_2 + Al_2(SO_4)_3 + 3H_2O = 3CaSO_4 + Al_2O_3 + 3H_2CN_2.$$

The solution is filtered from the precipitated calcium sulphate and aluminium hydroxide, and concentrated in a vacuum with the usual precautions, to prevent polymerization as much as possible to the dicyandiamide; and the cyanamide separated, and purified by solution in, and crystallization from ether.[1]

Cyanamide forms colourless crystals melting at 41° to 42° C. It is readily soluble in water, alcohol, and ether, but sparingly soluble in carbon disulphide, benzene, chloroform, and other organic solvents; the compound is deliquescent and attacks the skin like caustic alkalis. When heated above its melting-point it polymerizes with ease to dicyandiamide:

$$2CN_2H_2 = C_2N_4H_4.$$

And when heated to 150° C. a further polymerization

[1] N. Caro, *Z. angew. chem.* (1910), **23**, 2405–17; *J.S.C.I.*, **30**, 23.

takes place with formation of tricyantriamide or melamine : [1]

$$3C_2N_4H_4 = 2C_3N_6H_6.$$

The solution slowly polymerizes in the cold to dicyandiamide and the change takes place more quickly on boiling, particularly in the presence of ammonia, or other alkali.

When reduced in solution by means of zinc and hydrochloric acid, ammonia and methylamine are produced. The formation of the latter body is probably due to secondary reaction by reduction of the hydrocyanic acid first formed ; the reaction taking place in two stages, thus :

$$(1)\ CN_2H_2 + H_2 = HCN + NH_3$$
$$\text{and } (2)\ HCN + H_4 = CH_3NH_2.$$

Cyanamide unites directly with glycocoll to form glycocamine ; and with methyl glycocoll to form creatine. Heated to a high temperature with ammonium chloride it forms guanidine hydrochloride :

$$CN_2H_2 + NH_4Cl = C(NH)(NH_2)_2HCl.$$

With ammonium thiocyanate guanidine thiocyanate is obtained in a similar manner.

By the action of mineral acids, and certain organic acids, cyanamide combines with the elements of water to form urea :

$$CN_2H_2 + H_2O = CO(NH_2)_2.$$

Nitric acid added to an ethereal solution of the compound forms a crystalline precipitate of urea, which is insoluble in ether.

Dicyandiamidine sulphate may be obtained by adding commercial calcium cyanamide with good stirring to sulphuric acid mixed with twice its volume of water, and treating the product with hot water.

Additional compounds are formed with the haloid acids : thus when dry hydrochloric acid is passed into an ethereal solution of cyanamide, the compound

[1] Drechsel, *J. pr Chem.* [2], 13, 331.

CN_2H_22HCl is obtained, which may be crystallized from water in large plates.[1] With hydrogen sulphide, or ammonium sulphide, thiourea is formed; and it also combines with potassium cyanate to form monopotassium amidodicyanate,[2] and with guanidine to form diguanide.

Metallic monoderivatives may be prepared by the action of alkalis or alkaline earths on the cyanamide. Metallic diderivatives may be obtained by heating certain metallic cyanates:

$$Ca(CNO)_2 = CaCN_2 + CO_2 \text{ (Drechsel).}$$

By heating dry barium cyanide, when part of the cyanide is converted into cyanamide:

$$Ba(CN)_2 \rightleftharpoons BaCN_2 + C.$$

And by heating calcium carbide in an atmosphere of nitrogen to a high temperature; or by gently igniting calcium ferrocyanide:

$$Ca_2Fe(CN)_6 = 2CaCN_2 + Fe + N_2 + 4C.$$

The sodium salt may be prepared by the action of sodium amide on fused sodium cyanide:

$$NaNH_2 + NaCN = Na_2CN_2 + H_2.$$

This salt may be obtained as a crystalline powder, very soluble in water and alcohol, but insoluble in ether. It absorbs carbon dioxide from the air to form cyanamide carboxylic acid $CO\begin{matrix}NHCN\\ONa\end{matrix}$. The compounds Hg_2CN_2; $PbCN_2$; $CuCN_2$; and Ag_2CN_2, have been described. The latter body is an amorphous yellow precipitate, insoluble in ammonia but easily soluble in nitric acid, and when heated it explodes violently[3] with formation of metallic silver, nitrogen, and cyanogen.

Silver cyanamide is easily soluble in alkaline cyanides, and if silver nitrate be added to the solution, a crystal-

[1] Drechsel, *J. pr Chem.* [2], 9, 284.
[2] Mulder, *Ber.*, 6, 1236.
[3] H. R. Ellis *Chem. News*, 100, 154–55.

line double salt of silver cyanamide and cyanide is obtained; pure normal silver cyanamide is, however, only prepared by the precipitation of very dilute solutions, with stronger solutions a precipitate containing varying amounts of silver is obtained.[1]

By passing carbon dioxide through a boiling solution of sodium cyanamide in alcohol, an amorphous precipitate separates of the sodium salt of cyanamide carboxylic acid, CN_2NaCO_2Na, and the potassium, and other salts may be prepared in a similar manner thus: $(CN_2CO_2)Ca5H_2O$ white needles sparingly soluble in water and $(CN_2CO_2)Sr2\frac{1}{2}H_2O$. The acid when liberated splits into cyanamide and carbon dioxide; and the sodium salt when fused is converted into sodium cyanate:[2]

$$CN_2CO_2Na_2 = 2NaCNO.$$

DICYANDIAMIDE, $H_4C_2N_4$, a polymeric compound of cyanamide, from which it may be readily obtained by boiling the aqueous solution with an alkali, preferably ammonia.[3]

It crystallizes from its aqueous solution in broad laminæ, and is soluble also in alcohol, but is insoluble in ether, in which property it is distinct from cyanamide which is very soluble.

On heating to 150° C. normal malamine is formed together with melam and ammonia.

When heated with ammonium carbonate solution to 120° C. or with water, ammelide (melanurenic acid) is produced.

When heated with concentrated ammonia in sealed tubes to 120° C. for three hours, melamine and ammeline are produced; and when fused with alkali hydroxide at 500° C. dialkali cyanamides are produced:

$$4NaOH + C_2H_4N_4 = 2N_2CNa_2 + 4H_2O.$$

Guanylurea is formed when dicyandiamide is heated

[1] N. Caro, etc., *J.S.C.I.*, **30**, 23.

[2] G. Meyer, *J. pr. Chem.*, **126**, 419. [3] Haag, *A.*, **122**, 22.

with dilute acids by combination with the elements of water :

$$C_2N_4H_4 + H_2O = CONH_2NHC(NH)NH_2.$$

Concentrated sulphuric acid acts on dicyandiamide liberating carbon dioxide, and ammonia, and forming guanidine ;[1] and guanylthiourea is produced by heating with hydrogen sulphide. On reduction with nascent hydrogen in acid solutions, melamine, and ammonia, are produced.[2]

When heated with ammonium chloride to 150° C. carbon dioxide and ammonia are evolved, and guanidine hydrochloride formed, and it combines with hydrothiocyanic acid to form thioammeline :

$$(CN)_2(NH_2)_2 + HCNS = (CN)_3(NH_2)_2HS.$$

Heated on the water bath with hydrazine hydrate guanazole is obtained, which when heated to 270° C. for half an hour is converted into pyroguanazole with evolution of ammonia. The pyroguanazole separates from solution in strong hydrochloric acid with two molecules of acid, and from dilute solutions, with one molecule of HCl.[3]

Diguanides may be obtained by heating dicyandiamide with the hydrochlorides of aromatic amines in aqueous solutions. When heated with aniline hydrochloride, phenyl diguanide is produced.[4]

β-methylguanidine dicyandiamide is produced by the action of thiocarbamide and methylamine in presence of mercuric oxide.[5]

A sodium salt of dicyandiamide is produced by mixing an alcoholic solution of the compound with sodium ethylate, as a crystalline precipitate.[6] It forms the compounds $C_2N_4H_4AgNO_3$; $(C_2N_4H_4)_2AgNO_3$; $(C_2N_4H_4)_3AgNO_3$; when mixed with silver nitrate solution in the molecular proportions of 1 : 1 ; 2 : 1 ;

[1] H. Lidholm, *Ber.* (1913), **46**, 156–160.
[2] Ralhke, *Ber.* **18**, 3607.
[3] K. A. Hofmann and O. Ehrhard, *Ber.* (1912), **45**, 2731–40.
[4] Luminère and Parrin, *A.* (1905), i. 249.
[5] *J.C.S.*, i. 842, 1911. [6] Bamberger, *Ber.*, 16, 1461.

3 : 1. The first compound is converted by caustic soda solution into the silver salt, $C_2H_3N_4Ag$, while the second, and third, yield the same compound together with silver oxide. On boiling the silver salt with water, it is converted first into silver cyanamide and ultimately into cyanamide.[1]

Dicyandiamide (cyanoguanidine) does not possess the poisonous properties of cyanamide and is said to be harmless to mice. The nitrocompound is used in the manufacture of explosives.

From a study of the reactions and decompositions of the compound, H. Lidholm [2] considers it to possess the structure of guanidinoformonitrile:

$$NH : C(NH_2)NH : CN.$$

DICYANDIAMIDINE (guanyl carbamide), $C_2H_6ON_4$, may be prepared by evaporating a solution of dicyandiamide with a moderately strong solution of sulphuric acid, or by treating calcium cyanamide with the acid diluted with twice its volume of water.

Commercial calcium cyanamide is gradually added to a solution of 33 per cent. sulphuric acid, a vigorous action sets in with evolution of gas. The cooled product is then treated with hot water, and the filtered aqueous solution concentrated. Sulphate of calcium first separates out and then crystals of dicyandiamidine sulphate, $(C_2H_6ON_4)_2H_2SO_4 2H_2O$, contaminated with the sulphates of calcium and ammonium; but may be purified by recrystallization from alcohol.

The crystals are soluble in water, and alcohol, but are insoluble in ether, and lose all water at 110° C. By treating the solution with barium chloride dicyandiamidine chloride $(C_2H_6ON_4)HCl\frac{1}{2}H_2O$, may be obtained [3] in thin colourless leaflets.

The sulphate is decomposed by barium hydroxide forming dicyandiamidine or guanyl carbamide, which, when crystallized from alcohol, forms lustrous prisms,

[1] N. Caro and B. Schück, *Z. angew. Chem.* (1910), **23**, 2405.
[2] *Ber.* (1913), **46**, 156–60.
[3] T. Jona, *Gazz.* (1907), **37** [ii], 558–62.

which rapidly absorb carbon dioxide from the air. The free base melts at 105° C. and gives off ammonia on boiling with water, or at 160° C.

The addition of an ammoniacal solution of cupric sulphate produces first a violet colour and then precipitates a rose red cupric compound, $C_4H_5O_2N_4Cu$. This precipitate is also formed when a solution of a copper salt is added to a solution of the dicyandiamidine containing sodium hydroxide. An insoluble precipitate with nickel is also formed, but not with the other metals of the same group, and may, therefore, be used in the quantitative determination and separation of nickel.[1]

The picrate crystallizes in yellow plates, melting-point 265° C., and is used for the quantitative determination of the compound.[2] Dicyandiamidine chloroplatinate, $(C_2H_5ON_4)_2H_2PtCl_6$, is crystalline, and the palladium dicyandiamidine, $Pd(C_2H_5ON_4)_22H_2O$, is obtained by the reaction of dicyandiamidine sulphate, caustic potash, and palladium chloride, as a yellow crystalline powder [3] soluble in ammonia.

The sulphate heated with acetic anhydride yields $C_2H_5ON_4SO_3H$ guanylcarbamidesulphonic acid, which crystallizes in prisms; the ammonium salt forms short thick prisms. Melting-point, 165° to 167° C.

When heated with acetic anhydride and sulphuric acid it is converted into acetylguanylcarbamide, or acetyldicyanodiamidine.[4]

Dicyandiamidine chloride condenses with dextrose in alcoholic solutions to form dicyandiamidine dextrose,

$$OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_4{\cdot}CH : N{\cdot}C(NH){\cdot}NHCO{\cdot}NH_2HCl,$$

in slender microscopic needles, melting-point 107° C., at which temperature it begins to decompose.[5]

NORMAL MELAMINE, $C_3H_6N_6$ (cyanuramide), is

[1] H. Grosmann and B. Schück, *Ber.*, 43, 674–6.
[2] *J.C.S.* (1910), i. 14. [3] Grossman and Schück, *l.c.*
[4] T. Jona, *Gazz.* 38 [ii], 480–84.
[5] L. Radlberger, *J.C.S.* (1913), i. 450.

obtained when dicyandiamide is heated to 150° C., and like the latter body it is a polymeride of cyanamide :

$$3C_2H_4N_4 = 2C_3H_6N_6.$$

It is also found among the products formed by the action of heat on ammonium thiocyanate.[1] And by the action of ammonia on cyanogen chloride at 100° C.[2]

Melamine is obtained in monoclinic prisms which may be sublimed unchanged by gentle heating. It is very slightly soluble in hot or cold water, or alcohol, but dissolves in glycerine ; it is a powerful base and forms salts with acids. When heated to redness it is converted into mellen, and by boiling with dilute nitric acid it is ultimately converted into cyanuric acid.[3]

The carbonate crystallizes in needles and forms the platinochloride, $(C_3H_6N_6HCl)_2PtCl_42H_2O$.[4] The sulphate, $(C_3H_6N_6)_2H_2SO_42H_2O$, is very sparingly soluble in cold water.[5] The crystalline compound, $C_3H_6N_6AgNO_3$, may be obtained by the addition of silver nitrate, which is soluble in hot water, and by treatment with ammonia, the compound, $(CN)_3(NHAg)_2NH_2$, is said to be obtained.[6]

Melamine and dextrose heated in 30 per cent. alcoholic solution on the water-bath condense, yielding a product consisting of two molecules of melamine to one of dextrose :

$$[C_3N_3(NH_2)_2{\cdot}NH]_2CH\,[CHOH]_4CH_2{\cdot}OH.$$

The compound crystallizes in lustrous crystals which do not reduce Fehling's solution, and melt at 281° C.[7]

When melamine is heated with a large proportion of hydrazine hydrate for five hours under pressure at 150° C. microscopic needles of triaminomelamine are

[1] Liebig, *A.*, **10**, 18 ; **53**, 242 ; Volhard, *J. pr Chem.* [ii], 929 ; Claus, *A.*, **179**, 121 ; *B.*, **9**, 1915.

[2] Hofmann, *Ber.*, **18**, 2765. [3] Knapp, *A.*, **21**, 256.

[4] Hofmann, *Ber.*, **18**, 2760.

[5] Dreschsel, *J. pr Chem.* [ii], **13**, 322. [6] Zimmermann.

[7] L. Radlberger, *Chem. Zentr.* (1913), i. 2110 ; *J.C.S.* (1913) i. 960.

obtained, this product rapidly reduces warm ammoniacal silver nitrate solution.[1]

Of the four isomeric melamines theoretically possible only two alkylmelamines are known: the normal melamine, derivatives of the compound described above, and isomelamine. According to Hans Krall [2] this latter body may be isolated by heating guanidine carbonate at 180° C. for three hours when a mixture is obtained of ammeline and isomelamine, the latter is separated by treatment with a cold aqueous solution of sodium hydroxide in which the ammeline dissolves.

ISOMELAMINE is said to crystallize in ill-defined crystals. With strong acids isomerization takes place, with formation of the corresponding salt of ordinary melamine; and when isomelamine is heated to 260° C. normal melamine is formed.

GUANIDINE, $CN_3H_5 = NH.C(NH_2)_2$, is formed when ammonium thiocyanate is heated to 190° C. Thiourea is first formed which is then converted into guanidine thiocyanate. It may also be produced by the interaction of ammonia and cyanamide:

$$CN_2H_2 + NH_3 = CN_3H_5.$$

And by the action of cyanogen chloride, bromide or iodide on alcoholic ammonia, cyanamide being first formed, thus: [3]

(1) $CNI + 2NH_3 = NC{\cdot}NH_2 + NH_4I$
(2) $NC{\cdot}NH_2 + NH_4I = (NH_2)_2C : NHHI.$

Guanidine salts may be obtained by heating together dicyandiamidine, or melamine, with the corresponding ammonium salt;[4] or by heating dicyandiamide in presence of water under pressure.[5]

Guanidine nitrate may be obtained in good yield by treating dicyandiamine with an acid mixture

[1] Stollé and Krauch, *Ber.* (1913), **46**, 2337–39.
[2] *P.C.S.* (1913), p. 377. [3] Erlenmeyer; M. Schenck.
[4] G.P. 222,552 (30.10.08), Stickstoffwerke.
[5] E.P. 815 (12.1.10), S. J. Gelhār.

containing 25 per cent. hydrochloric acid (sp. gr. 1.19), and 35 per cent. nitric acid (1.38 sp. gr.).[1]

Guanidine is most conveniently prepared as the thiocyanate by heating dry ammonium thiocyanate. The method usually applied is to heat the dry salt to 180° to 190° C. for twenty to twenty-four hours. According to Hans Krall,[2] the best method for the preparation of the compound is to heat the ammonium thiocyanate to 200° C. when a yield of 60 per cent. may be obtained in four hours. It is suggested that the guanidine thiocyanate is formed by the interaction of cyanamide and some unchanged ammonium thiocyanate :

$$CN_2H_2 + NH_4CNS = HN{\cdot}C(NH_2)_2HCNS,$$

And that the cyanamide is formed by the decomposition of the thiourea which is first formed, with evolution of hydrogen sulphide :

$$(1)\ NH_4CNS = CS(NH_2)_2$$
$$(2)\ CS(NH_2)_2 = CN_2H_2 + H_2S.$$

The guanidine thiocyanate may be purified by recrystallization from alcohol, or water.

Guanidine is a strongly alkaline crystalline substance which absorbs carbon dioxide from the air, and forms crystalline salts with acids. It is found among the products resulting from the oxidation of certain proteid substances such as egg albumen.

Guanidine perchromate [3] may be prepared by heating guanidine carbonate and chromic acid in water, and then treating the mixture with hydrogen peroxide at 0° C. The perchromate separates out in brownish yellow prisms which are very stable when dry, and do not explode. When boiled with water the chromate, $(CN_3H_5)_2H_2CrO_4.H_2O$, is formed in thin yellow monoclinic crystals.

Guanidine carbonate, when treated with cobaltisodium nitrite solution at 50° C. yields guanidinium

[1] N. Caro and others, *J.S.C.I.*, 30, 25.
[2] *P.C.S.* (1913), **166** ; *T.C.S.*, **150**, 1913, 1275.
[3] K. A. Hofmann, *Ber.*, **62**, 2773–76.

trihydroxotrinitrocobaltate, $[Co(HO)_3(NO_2)_3](C.H_6N_3)_3$, in long red prisms, which are decomposed by water at 80° C. As guanidine can be produced by the action of cyanogen iodide on alcoholic ammonia, so also may guanidine derivatives be obtained by substituting organic ammonias. Thus with cyanogen iodide and alcoholic methylamine s-dimethylguanidine is obtained and in a similar manner the compounds, ethyleneguanidine, prophyleneguanidine, etc., may be prepared.[1]

Mono and s-dimethylguanidine may be obtained by the action of methyliodide on guanidine sulphate and potassium hydroxide.[2] Guanidine reacts with the esters of monobasic acids forming simple acylguanidines ;[3] thus formylguanidine, $H_2NC(:NH)NHCHO$, may be prepared by adding to ethyl formate, a dilute alcoholic solution of guanidine. It is obtained in crystalline granules ; in cold aqueous solution bromine converts it into formylbromoguanidine, $C_2H_4ON_3Br$. From ethyl acetate in a similar manner acetylguanidine may be obtained.

Aminoguanidine nitrate when diazotized in aqueous solution at 0° C. with sodium nitrite yields aminoguanidine diazohydroxide, $C_2H_7N_{10}OH$, in colourless crystals which explode when struck, or on heating to 135° to 140° C. The chloride, $C_2H_7N_{10}Cl$, is obtained in colourless silky needles which explode at 140° C., and couples slowly with aromatic amines.[4]

If the compound is diazotized in acid solutions, using nitrous vapour carbamideimidazide $H_2NC(:NH)N_3$, is formed ;[5] by the action of strong reducing agents it is converted into tetrazylhydrazine, $H_2NNHCHN_4$.

Amidoguanidine diazonitrate reacts with excess of silver nitrate to form $C_2H_7N_{10}OAg.AgNO_3 3H_2O$ in light yellow needles or prisms. It reacts with hydriodic acid to form the compound $C_2H_7N_{10}I$, in light yellow

[1] M. Schenck, *Arch. Pharm.* (1909), **247**, 490–506.
[2] M. Schenck. [3] W. Traube, *Ber.*, **43**, 3586–90.
[4] K. Hofmann and R. Roth, *Ber.* (1910), **43**, 682.
[5] Thiele, *Ann.*, **270**, 46.

explosive needles, and $C_2H_7N_{10}I_4$, in almost black crystals with a dark green lustre.[1]

DIGUANIDE (guanylguanidine),

$$C_2H_7N_5 = NH[C(NH_2) : NH]_2$$

may be prepared by heating an intimate mixture of dicyandiamide and ammonium chloride.[2] The substitution of ammonium bromide, or better still ammonium iodide is recommended by O. Ostrogovich,[3] whereby the yield of diguanide is said to be raised from 21 to 45 per cent.

Finely powdered and dry dicyandiamide and ammonium iodide are intimately mixed and heated to 173° C. for five minutes, the cooled product is dissolved in water, filtered and made alkaline with aqueous ammonia and then ammoniacal copper sulphate solution added so long as the rose-coloured precipitate of the copper compound of dicyandiamidine is precipitated. Further addition of the copper solution precipitates a violet compound of the diguanide.

The diguanide may be obtained from the copper derivative, by treatment with dilute sulphuric acid, and the pure base from the latter solution by barium hydroxide. The salt may be purified by crystallization from alcohol in glistening prisms which melt at 130° C., but the aqueous solution of the compound decomposes gradually on heating.

The following salts have been described by K. Rackmann.[4] The carbonate, $C_2H_7N_5H_2CO_3$, crystallizes in prisms sparingly soluble in alcohol; the hydrochloride, $C_2H_7N_5 2HCl$, in glistening needles which melt at 248° C.; the nitrate, $C_2H_7N_5HNO_3$, in large glistening prisms, melting-point 192° C.; the acetate, $C_2H_7N_5CH_3CO_2H$, melting-point 268° C.; and the oxalate, $C_2H_7N_5C_2O_4H_2$, melting-point 210° C.

When the chloride is treated with dextrose in

[1] K. Hofmann, *Ann.*, **380**, 131, 47.
[2] Bamberger and Dieckmann, *Ber.*, **25**, 545.
[3] *Chem. Zentr.* (1910), **11**, 1890.
[4] *Annalen* (1910), **376**, 163.

alcoholic solutions condensation takes place and guanylbiguanidine dextrose :

$$OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_4{\cdot}CH : N{\cdot}C(NH){\cdot}NH{\cdot}C(NH){\cdot}NH_2{\cdot}2HCl$$

is obtained in small needles, which yield red needles of cuprobiguanide sulphate with ammoniacal copper sulphate.

By substituting the hydrochloride of aromatic amines for the ammonium salt in the preparation of diguanide, aromatic diguanides may be obtained ; thus aniline hydrochloride and dicyandiamide yield phenyldiguanide, etc., etc.[1]

NORMAL AMIDO DICYANIC ACID. This compound is formed when dicyandiamide is heated with barium hydroxide solution, one of the amido group, of the dicyandiamide is replaced by hydroxyl. It may also be formed by the direct combination of potassium cyanate and cyanamide, when a solution of these two bodies is left for some time,[2] the acid being obtained as its potassium salt.

The acid is monobasic and crystallizes in needles. It is decomposed when its solution is heated alone, or with sulphuric acid by combination with a molecule of water to form biuret :

$$(CN)_2NH_2OH + H_2O = NH_2{\cdot}CO{\cdot}NH{\cdot}CONH_2.$$

With ammonium sulphide thiobiuret is produced.[3]

MELAM. When dry ammonium thiocyanate is heated to 300° C. hydrogen sulphide, carbon disulphide, and ammonia are evolved. If the heating is continued until the evolution of gas ceases, crude melam thiocyanate is formed together with other products. The residue is first washed with hot water, then with a cold dilute solution of potassium hydroxide, and finally dissolved in dilute hydrochloric acid and reprecipitated by potassium hydroxide solution.

It is an insoluble white powder, which evolves

[1] G. Cohn, *J. pr Chem.* (1911) [ii], **84**, 394–400 ; *J.C.S.* (1911), i. 928.

[2] Hallwack, *A.*, **153**, 295. [3] Baumann, *Ber.*, **8**, 709.

ammonia when heated; when boiled with dilute acids or alkalis it yields ammonia and ammeline, with concentrated nitric acid cyanuric acid is formed. Mellem, $C_6H_6N_{10}$, is a constituent of crude melam formed by heating dry ammonium thiocyanate as described above. It may be separated from the melam by boiling with a 5 per cent. solution of potassium hydroxide for twenty-four hours, when the melam is converted into ammeline, bnt the mellen is left unacted on.

Mellen is a white odourless insoluble powder, which when boiled with concentrated potash solution is converted into ammelide and ammonia.

AMMELINE is obtained by boiling melam for some time with potassium hydrate solution. It is also formed together with melamine when dicyandiamine is heated with concentrated ammonia solution in sealed tubes for three hours at 120° C.[1]

It is very sparingly soluble in water, alcohol, or ether, and when heated with equal quantities of hydrazine hydrate for five hours under pressure to 130° C. diaminoammeline is obtained in prisms which melt above 340° C.[2]

AMMELIDE (melanurenic acid). Liebig considered ammelide and melanurenic acid as two distinct bodies to which he gave the formulæ,

$C_6N_9H_9O_2 : 3(CNH_2N : CNHO)$ and $C_3N_4H_4O_2(CNH_2N.2CNHO)$

respectively. Gerhardt, however, considered them to be identical, an observation that was afterwards confirmed by Klasson,[3] who proved the identity of these bodies.

Ammelide may be prepared by heating melam with concentrated sulphuric acid to 190° C. for a short time, and pouring the product into a large excess of water, from which the sulphate slowly separates. It may also be formed as the principal product by the

[1] R. Stollé and K. Krauch, *Ber.* (1913), **46**, 2337.
[2] R. Stollé and K. Krauch, *l.c.*
[3] *J. pr Chem.* [2], **33**, 295.

action of fuming sulphuric acid at 190° C. on melamazine, $(C_3N_3NH_2)_2(NHNH)_2H_2O$, obtained by the action of hydrazine sulphate on dicyandiamide.[1]

It is a white powder, sparingly soluble in cold water, rather more so in hot water.

ISOAMMELINE and **ISOAMMELIDE** are known only as their alkyl derivatives, but have never yet been isolated, nor have any metallic derivatives been formed.

AZULMIC ACID. When cyanogen is passed into aqueous ammonia a dark brown flocculent precipitate rapidly forms together with oxamide and oxamic acid. The formula, $C_4H_5N_5O$, has been given to the compound.

A similar, and probably identical, product is obtained when a little alkaline cyanide (particularly potassium cyanide) is dissolved in an aqueous solution of hydrocyanic acid: the solution turns first yellow, then dark brown, and ultimately deposits dark brown flocks of the compound.

It is more rapidly formed by keeping a solution of calcium cyanide of over 20 per cent. strength for a few days. The cyanide solution is prepared by passing hydrocyanic acid into milk of lime, a solution of 30 per cent. turns brown in a few hours and rapidly deposits the compound together with a basic calcium cyanide.

But little is known of the constitution and properties of the compound. It is converted into an insolubie orange powder by nitric acid. It is soluble in concentrated sulphuric acid, and is very slightly soluble in water, but is soluble in alkalis, the solution exhibiting fluorescence, and is reprecipitated by acids.

When dry distilled ammonia and hydrocyanic acid are given off amongst other products.

Dry gaseous cyanogen and ammonia form a black body called hydrazulmin, which water is said to convert into azulmic acid with liberation of ammonia.

[1] K. Hofmann, etc., *Ber.* (1911), **44**, 2713.

CHAPTER III

SIMPLE CYANIDES

THE simple metallic cyanides are formed by a variety of reactions, and the hydrogen salt can be obtained from natural sources by the hydrolysis of the glucoside amygdaline, which splits up into glucose, benzaldehyde, and hydrocyanic acid :

$$C_{20}H_{27}NO_{11} + 2H_2O = C_7H_6O + HCN + 2C_6H_{12}O_6.$$

The following are among the general methods for the production of cyanides :

1. Fusion of an alkali metal ferrocyanide, with or without the carbonate of an alkali metal, or metallic sodium :

(*a*) $Na_4Fe(CN)_6 = 4NaCN + Fe + C_2 + N_2$.
(*b*) $Na_4Fe(CN)_6 + Na_2CO_3 = 5\,NaCN + NaCNO + Fe + CO_2$.
(*c*) $Na_4Fe(CN)_6 + Na_2 = 6NaCN + Fe$.

2. By dissolving cyanogen gas in a solution of caustic alkali, when equivalent quantities of cyanide and cyanate are formed, or by direct combination of the gas with metallic sodium :

(*a*) $(CN)_2 + 2KOH = KCN + KCNO + H_2O$.
(*b*) $(CN)_2 + Na_2 = 2NaCN$.

3. By distilling an aqueous solution of a ferrocyanide with a dilute acid, and absorbing the evolved vapour in a caustic alkaline solution :

(*a*) $2K_4Fe(CN)_6 + 3H_2SO_4 = 6HCN + FeK_2Fe(CN)_6 + 3K_2SO_4$.
(*b*) $6HCN + 6KOH = 6KCN + 6H_2O$.

4. By fusing nitrogenous organic matter with carbonate of potassium at a red heat, or by passing

nitrogen over a mixture of potassium carbonate and carbon heated to a very high temperature :

$$K_2CO_3 + 4C + N_2 = 2KCN + 3CO.$$

5. By the oxidation of thiocyanates with suitable oxidizing agents :

$$2HCNS + 3O_2 + 2H_2O = 2HCN + 2H_2SO_4.$$

6. By fusing an amide or cyanamide of an alkali metal with carbon :

$$(a)\ NaNH_2 + C = NaCN + H_2.$$
$$(b)\ Na_2CN_2 + C = 2NaCN.$$

7. In the destructive distillation of coal small quantities of hydrocyanic are formed.

8. By passing dry ammonia and carbon monoxide through red-hot tubes :

$$2NH_3 + CO = NH_4CN + H_2O.$$

9. By passing ammonia over charcoal heated to 1150° to 1180° C. :

$$2NH_3 + C = NH_4CN + H_2.$$

10. By passing ammonia and carbon disulphide vapour over red-hot iron, or copper :

$$2NH_3 + CS_2 + 4Cu = 2Cu_2S + NH_4CN + H_2.$$

11. And by the reduction of a fused nitrate with an excess of charcoal.

The cyanides of the alkali metals, and the alkaline earth metals are soluble in water; the sodium and potassium salt can be readily obtained in crystals by evaporating their aqueous solution; the barium, strontium and lithium cyanides crystallize with difficulty, while the solution of the calcium and magnesium salts cannot be evaporated; complete decomposition of these salts occurs when their solutions are heated, with evolution of hydrocyanic acid and precipitation of the metallic hydroxide. The ammonium salt also decomposes when its aqueous solution is heated, both ammonia and hydrocyanic being evolved. The cyanides of the heavy metals are for the most part insoluble

in water, the exceptions being mercury cyanide, which is fairly soluble, and cadmium cyanide, which is sparingly soluble.

Hydrocyanic acid is a weak acid and can readily be displaced from the solution of its alkali or alkaline earth metal salts by carbon dioxide or weak organic acids.

The solution of the alkali metal cyanides can be evaporated under ordinary atmospheric pressure with but little loss of hydrocyanic acid, and under reduced pressure with practically no loss; by continued boiling of the solution the reaction

$$KCN + 2H_2O = KHCO_2 + NH_3$$

takes place, but only to a small extent, this decomposition being by no means so great as is usually stated.

The insoluble cyanides of the heavy metals are quite stable; and although in the majority of cases they are readily decomposed by dilute acids, yet they remain unaltered in the air in the dry state, and on heating to 100° C.

Most of these insoluble cyanides have a great tendency to form double salts, some of which are of great stability and interest. These double cyanides can be divided into two series:

1. The simple double cyanides which may be easily decomposed by dilute mineral acids.

2. The complex double cyanides, which when heated with dilute mineral acids are decomposed only with difficulty or not at all.

The double cyanides of nickel or zinc are types of the first series, and the double cyanides of iron, cobalt or platinum types of the latter series.

The alkaline cyanides when fused with polysulphides or free sulphur are converted into thiocyanates. The same compound is produced when the cyanide solution is boiled with sulphur or a polysulphide:

$$NaCN + S = NaCNS.$$
$$4NaCN + Na_2S_5 = 4NaCNS + Na_2S.$$

And they are converted into ferrocyanides, by shaking or warming the solution of these salts with freshly precipitated ferrous hydroxide :

$$6KCN + Fe(OH)_2 = K_4Fe(CN)_6 + 2KOH.$$

This reaction is frequently used for detecting the presence of a soluble cyanide, the ferrocyanide being acidified and a ferric salt added when a blue colour is produced. This test may be obtained with any soluble simple cyanide except the mercury salt.

Aqueous cyanide solution containing free hydrocyanic acid gradually turns brown, and dark brown flocks are ultimately deposited of azulmic acid, the amount formed depending on the proportion of free hydrocyanic acid present. A solution of free hydrocyanic also darkens and turns brown in the presence of small traces of alkali for the same reason.

Aqueous cyanide solutions slowly decompose on keeping for some time, with formation of a formate and ammonia. This reaction takes place to a much greater extent with solutions of the alkaline earth cyanides, particularly the calcium salt. If a 25 per cent. solution of the latter is kept for a few days the solution becomes dark brown, and large quantities of ammonium cyanide may be evolved on warming the liquid.

A dilute solution of an alkaline cyanide dissolves several of the noble metals slowly in the presence of oxygen, or an oxidizing agent, to form double cyanides :

$$4NaCN + Au_2 + O + H_2O = 2NaAu(CN)_2 + 2NaOH.$$

This reaction is one that is adopted to a large extent in practice, and is in use in most of the gold producing centres ; it is for this purpose that practically all the cyanide made at the present time is used.

When fused in contact with dry air or with an easily reducible oxide such as lead oxide or manganese dioxide an alkaline cyanide is readily oxidized, one atom of oxygen combining with one molecule of the cyanide to form a cyanate :

$$2NaCN + O_2 = 2NaCNO.$$

This avidity for oxygen makes the cyanide an excellent reducing agent, for when fused with metallic oxides such as those of tin or lead, a button of the reduced metal is easily obtained :

$$PbO + KCN = Pb + KCNO.$$

The cyanates may also be produced in the wet way by oxidizing the solution with permanganate.

By fusing the cyanide in contact with moist air, ammonia is evolved and a carbonate left :

$$2NaCN + 3H_2O + O_2 = 2NH_3 + Na_2CO_3 + CO_2.$$

Hydrocyanic acid, the simple cyanides, and the simple double cyanides are extremely violent poisons, and in the preparation of hydrocyanic acid great care should be taken. The operation should only be performed in a draught cupboard under a well-ventilated hood, or in the open air. For a very small amount of the vapour, if allowed to escape into the room, the atmosphere of which is breathed for some time, is liable to produce nervous depression and violent headaches.

All simple cyanides, and simple double cyanides, and many of the complex double cyanides when boiled with mercuric oxide, or chloride, are converted into mercuric cyanide :

(1) $2NaCN + HgO + H_2O = Hg(CN)_2 + 2NaOH.$
(2) $2NaCN + HgCl_2 = Hg(CN)_2 + 2NaCl.$
(3) $K_4Fe(CN)_6 + 3HgO + 3H_2O = 3Hg(CN)_2 + 4KOH + Fe(OH)_2.$

The dry cyanides or double cyanides when ignited with concentrated sulphuric acid are completely destroyed, the oxides of sulphur and carbon being evolved and the sulphates of ammonia and the metals being left in the residue with the excess acid.

When chlorine is passed into a cyanide solution, cyanogen chloride and a chloride of the base is formed :

$$NaCN + Cl_2 = NaCl + CNCl.$$

Bromine, or iodine, act in a similar manner, and if the

cyanide solution is moderately strong, the liquid becomes pasty with the separated crystals of the cyanogen haloid.

Hydrogen sulphide passed into a strong aqueous solution of a cyanide forms chrysean.[1]

$$4NaCN + 4H_2S = C_4H_5N_3S_2 + NH_3 + 2Na_2S.$$

If sulphur dioxide is passed through a cooled 40 per cent. solution, hydrocyanic acid is liberated, and the liquid turns brown, and in a few days deposits crystals of cyanosulphite of potassium, SO_2CNK, or other alkali metal. A solution of this salt reduces the salts of silver and gold.

The action of picric acid, or of picrates on the easily decomposable cyanides results in the formation of isopurpurates. This action, however, does not take place with the cyanides of mercury, copper, or silver.[2]

Any metallic cyanide heated with potassium nitrate and chlorate detonates with great violence. The cyanides of the noble metals, when heated alone, decompose into the metal and cyanogen gas, a part of the latter generally polymerizing into more or less paracyanogen. Alkali metal cyanides are not affected by simple ignition out of air contact, but the alkaline earth cyanides are converted by this process into more or less cyanamide. Attempts to prepare calcium cyanide by a fusion process only result in the formation of calcium cyanamide. Substituting barium for the calcium both cyanide and cyanamide are obtained.

When powdered magnesium is ignited out of air contact with an alkaline cyanide, decomposition of the cyanide occurs, with formation of magnesium nitride :

$$2KCN + 3Mg = Mg_3N_2 + 2K + 2C.$$

Glucinium, calcium, boron, aluminium, cerium, and lanthanum act in a similar manner.[3]

[1] **Wallack**, *Ber.*, **7**, 902.

[2] R. Varet, *Compt. rend.*, **119**, 562 ; *J.S.C.I.*, **14**, 399.

[3] A. Vournasos, *Z. anorg. chem.* (1912), **77**, 191–96 ; *Bul. Soc. Chim.* (1911)[iv], **9**, 506–12.

If potassium cyanide in the solid state is added to commercial aldehyde at a temperature below 30° C., the solution becomes thick, due to the formation of potassium glycollate and hexamethylenetetramine :

$$10CH_2O + 4KCN + 2H_2O = (CH_2)_6N_4 + 4CH_2OHCOOK.$$

The glycollate may be isolated by precipitating with lead acetate, and decomposing the washed lead compound with hydrogen sulphide. If a solution of potassium cyanide is mixed with an equivalent proportion of calcium chloride and then slowly dropped into a formaldehyde solution, a white precipitate separates of a very unstable nitrogen free compound, and from the remaining solution calcium glycollate is obtained with evolution of nitrogen. No hexamethylenetetramine is formed in this case.[1]

According to K. Polstorff and H. Meyer,[2] if a 25 per cent. solution of potassium cyanide, and about 18 per cent. formaldehyde are mixed slowly at 6° C. and kept at atmospheric temperature for twenty-four hours, some ammonia is evolved and the solution then contains glycollic and iminodiacetic acid and nitrilotriacetic acid.

The solution when first mixed results in the formation of glycollonitril, which, on keeping the solution, is partly hydrolyzed into glycollic acid and partly converted into aminoacetonitrite. These two bodies then react to form iminodiacetic acid and nitrilotriacetic acid. The glycollic acid can be obtained by steam distillation, five to ten minutes after mixing the two solutions.

THE METALLIC CYANIDES

ALUMINIUM CYANIDE does not appear to have a separate existence; the addition of a soluble cyanide to an aluminium salt results in the precipitation of aluminium hydroxide with liberation of hydrocyanic acid. The same result is obtained with the simple

[1] *J.C.S.I.*, **19**, 282. [2] *Ber.* (1912), **45**, 1905–12.

double cyanides, the hydroxide being precipitated along with the metallic cyanide. In aluminium ferrocyanide, $Al_4[Fe(CN)_6]_3$, the cyanide may be considered to exist combined with the complex iron cyanide :

$$4Al(CN)_3 : 3Fe(CN)_2.$$

When dry cyanogen is passed over gently heated aluminium chloride, a brown liquid is produced with considerable development of heat which crystallizes on cooling and is decomposed by water with violence.[1]

AMMONIUM CYANIDE, NH_4CN, may be prepared in solution by passing hydrocyanic acid into aqueous ammonia, or by decomposing barium cyanide solution with ammonium sulphate, or the calcium salt with ammonium carbonate. It is prepared in the dry state by gently heating finely powdered potassium cyanide or ferrocyanide with ammonium chloride :

$$K_4Fe(CN)_6 + 6NH_4Cl = 4KCl + FeCl_2 + 6NH_4CN,$$

and condensing the vapour in a receiver cooled with a freezing mixture. It may also be prepared by passing dry ammonia over strongly ignited carbon.

It is obtained in the solid state in the form of colourless crystalline cubes, frequently grouped on the surface of the condenser in beautiful leaf-like patterns. It is very soluble in water and alcohol, and smells strongly of both ammonia and hydrocyanic acid,

The solid compound boils at 36° C. with dissociation into ammonia and hydrocyanic acid, the vapour being inflammable, burning with a bluish flame. It is very unstable in air, especially when heated, and both in the solid state and in solution it gradually changes into the brown azulmic acid and is energetically decomposed by chlorine or bromine with formation of the corresponding halogen cyanide. From the solution the whole of the compound may be driven off as ammonia and hydrocyanic acid by boiling.

BARIUM CYANIDE, $Ba(CN)_2 2H_2O$, may be obtained by passing hydrocyanic acid into a solution of barium

[1] G. Perrier, *Compt. rend.* (1895), **120**, 1423–26.

hydroxide, or together with some cyanamide by igniting dry barium ferrocyanide out of air contact, and extracting the melt with water. This salt was at one time made on a large scale, as a preliminary to the preparation of alkaline cyanides by the process of Margueritte and De Sourdeval,[1] by passing air over a red-hot mixture of carbon and barium oxide.

When a solution of this salt is evaporated under ordinary atmospheric pressure a considerable proportion of the combined hydrocyanic acid is evolved, which also occurs, though to a much smaller extent, when the solution is evaporated under vacuum, and the product is therefore difficult to prepare free from oxide. The dry cyanide fuses at about 600° C.

When the solid is heated to 300° C. in the presence of steam, the whole of the nitrogen is evolved in the form of ammonia, leaving a residue of barium formate :

$$Ba(CN)_2 + 4H_2O = Ba(CO_2H)_2 + 2NH_3.$$

The compound, $BaCN(OCH_3)CH_3OH$, is obtained when hydrocyanic acid is passed into barium oxide in methylic alcohol.[2]

The aqueous solution readily dissolves the insoluble cyanides of many of the heavy metals to form a number of crystalline double salts, from which many others of the same series can be obtained by double decomposition with the corresponding sulphate.

BISMUTH CYANIDE has not yet been isolated. Bismuth hydroxide and hydrocyanic acid only result when an alkaline cyanide is added to a bismuth salt.

CADMIUM CYANIDE, $Cd(CN)_2$, may be prepared by decomposing barium cyanide with cadmium sulphate, or by adding a solution of an alkaline cyanide to an excess of a solution of a cadmium salt : it is sparingly soluble in water, from which it crystallizes in small colourless rhombic prisms, which are quite permanent in the air, but decompose when heated to 200° C.

[1] *Compt. rend.*, 50, 1100.

[2] Drechsel, *J. für Chem.* [2], 21, 77, 1880.

The oxycyanide, $Cd(CN)_2.CdO.5H_2O$, may be obtained by dissolving cadmium hydroxide in the cyanide solution.

The cyanide combines with other cyanides, forming a series of double salts. With potassium cyanide it forms the salt, $K_2Cd(CN)_4$, which is very soluble in water and permanent in the air, and crystallizes in octahedra. The solution gives precipitates with most metallic salts, thus with nickel and silver salts a white precipitate is obtained, the latter soluble in excess: and with ferrous salts a yellow precipitate. The double mercury salt, $Cd(CN)_23Hg(CN)_2$, crystallizes in white rectangular prisms permanent in the air, and readily soluble in water; and the double salts $2Cd(CN)_2Cu(CN)_2$ and $Cd(CN)_22Cu(CN)$ have been described, both of which are stable.

CALCIUM CYANIDE is known only in solution. Solid double salts, however, may be obtained with the cyanides of the heavy metals, and a basic cyanide is also known.

A solution of the salt may be readily prepared by passing hydrocyanic acid into milk of lime and a solution may be thus obtained of 30 to 35 per cent. calcium cyanide, but such a solution is exceedingly unstable; it smells strongly of hydrocyanic acid, and cannot be kept unchanged for more than an hour or so. The solution quickly turning brown, and depositing dark brown flocks of azulmic acid and crystals of a sparingly soluble basic cyanide of calcium; a considerable proportion of ammonium cyanide is also formed in solution. Thus a dark brown solution of the strong cyanide that has been kept stoppered for some time, when carefully distilled into a cooled glass receiver, will yield a large quantity of ammonium cyanide, which will crystallize in the condenser in beautiful fern-like patterns.

A solution of 15 per cent. or under of calcium cyanide may be kept if out of air contact for years without change, but a solution of any strength above this figure will rapidly turn brown and decompose in the

manner described, the rate of decomposition depending directly on the strength; the stronger the solution the quicker the decomposition. A solution of 20 per cent. strength may be kept for a day without discoloration, while a 30 per cent. solution turns brown in a few hours.

A solution of calcium cyanide of any strength, when boiled, evolves the whole of its cyanogen in the form of hydrocyanic acid, a heavy precipitate of calcium hydroxide forming in the liquor:

$$Ca(CN)_2 + 2H_2O = 2HCN + Ca(OH)_2,$$

a small portion of brown azulmic acid being also formed. This decomposition also occurs when the solution is boiled under reduced pressure.

Calcium cyanide does not appear to exist in the dry state, it cannot be obtained by evaporation and crystallization of the aqueous solution, and when calcium ferrocyanide is dried and heated out of air contact, calcium cyanamide only is formed and no cyanide:

$$Ca_2Fe(CN)_6 = 2CaCN_2 + Fe + 4C + N_2.$$

Calcium cyanamide is also the only nitrogen product that is formed when nitrogen is passed over heated calcium carbide:

$$CaC_2 + N_2 = CaCN_2 + C.$$

A basic salt of the composition $Ca(CN)_2 3CaO 15H_2O$ is produced by treating a warm and moderately strong solution of calcium cyanide with excess of lime filtering and allowing the liquor to cool. Small crystals of the basic salt then crystallize out.

Moderately stable double salts of calcium cyanide and the cyanides of the heavy metals are known. The double silver and the double copper salts may be obtained in crystals, the double calcium zinc cyanide is uncrystallizable, but the solution may be evaporated with but slight decomposition, and may be kept indefinitely in a stoppered bottle without decomposition.

CEROUS CYANIDE is unstable, the precipitate obtained by the action of an alkaline cyanide solution on a cerous salt decomposes immediately into a precipitate of cerous hydroxide and hydrocyanic acid.

CHROMIUM CYANIDE. No simple cyanide of this metal has yet been isolated; the precipitate which is first formed when a soluble cyanide is added to a chromium salt rapidly decomposes, forming a chromocyanide.

POTASSIUM CHROMOCYANIDE is best prepared by digesting freshly precipitated chromium carbonate, with potassium cyanide solution out of air contact; the evaporated liquor then yields yellow needles of the double salt, $K_4Cr(CN)_6$.[1] This salt is unchanged in the air at ordinary temperatures, but is decomposed on boiling, and on oxidation forming a chromicyanide. It yields precipitates with a number of metallic salts, and with ferrous salts a red coloration is obtained, said to be sufficiently characteristic to detect the presence of one ten-thousandth part of a ferrous salt.

POTASSIUM CHROMICYANIDE, $K_3Cr(CN)_6$, may be prepared by oxidizing the chromocyanides, or by heating potassium cyanide solution with a chromium salt in air contact. It crystallizes in yellow monoclinic crystals soluble in water, but insoluble in alcohol, and readily decomposed by acids. A solution of the potassium salt gives a series of precipitates with solutions of the heavy metals.

According to Descamp,[2] salts similar in constitution to the nitroferrocyanides may be obtained by passing nitric oxide into a solution of a chromocyanide.

A remarkable compound of chromium tetroxide and potassium cyanide, and having the composition expressed by the formula CrO_43KCN, has been described by O. F. Wiede.[3] It may be prepared by heating 5 grm. of the compound CrO_43NH_3, 6 grm. of potassium cyanide, and 30 grm. of water to 60° C. After cooling and filtering, the addition of alcohol

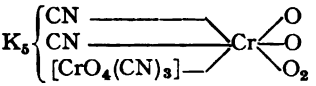
[1] *Moissan, Ann. Chem. Phys.* [6], **4**, 136.

[2] *Ann. Chem. Phys.* [5], **27**, 17.

[3] *Ber.* (1899), 32 [3], 378–87.

precipitates a reddish brown oil, which on standing deposits the compound in crystals. The crystals must be handled with care, for they are liable to explosion by pressure, friction, shock, or by rapidly heating to 115° C.[1]

A series of complex cyanogen compounds of the higher oxidation compounds of chromium are known. The composition of these bodies corresponds to the formulæ $K[CrO_4(NH_3)_2CN]$; $K_3[CrO_4(CN)_3]$; and $K_5[(CrO_4)_2(CN)_5]$. The latter salt is said to have the constitution :[2]



COBALT CYANIDE. The addition of a soluble alkaline cyanide to a cobalt solution produces a light pinkish coloured precipitate, which on washing undergoes change and turns brownish in colour. The precipitate will dissolve in excess of the alkaline cyanide, and if the solution is kept cool it turns deep red. The addition of alcohol precipitates a cobaltocyanide of the alkali metal. The potassium salt is obtained by these means in red deliquescent needles insoluble in ether and alcohol. Another method[3] by which the potassium salt may be prepared is to dissolve 10 parts of cobalt sulphate or chloride in 100 parts of water saturated with sulphur dioxide and cooled to 0° C. : potassium cyanide solution is then added until the red precipitate just redissolves. The pure metallic cobaltocyanides may be obtained by saturating the metallic solution with sulphur dioxide, thus with zinc an intensely orange-red precipitate is obtained, which is soluble in excess, with a dark red colour. The precipitate, when dried in a current of hydrogen, has an orange colour, but on heating it loses water and turns

[1] *J.S.C.I.*, **18**, 371.

[2] E. H. Riesenfeld, *Ber.*, **41**, 3536–52.

[3] E. P. Alvarez, *Ann. Chim. anal.* (1910), **15**, 129–31 ; *J.C.S.* (1910), ii. 454.

violet, and when moistened it resumes its original colour. Nickel salts saturated with sulphur dioxide yield a yellow precipitate which turns green on warming, and is soluble in excess of the reagent with a yellow colour. The addition of tartaric acid destroys the yellow colour. Cobalt salts treated in a similar manner yield a red precipitate which dissolves in excess of the reagent with a red colour.

The cobaltocyanides are very unstable, particularly in solution, and rapidly absorb oxygen to form cobalticyanides; by heating the solution the transformation proceeds rapidly with evolution of hydrogen.

Hydrocobaltocyanic acid may be prepared by the action of hydrogen sulphide on the lead salt, or of dilute sulphuric acid on the barium or lead salts, and precipitation from the solution by alcohol. It is very unstable.

Compounds similar to the nitroferricyanides are said to be obtained by passing nitric oxide into the cobaltocyanide solution.[1]

COBALTICYANIDES. These complex but stable salts may be prepared by dissolving cobaltous cyanide or oxide in potassium cyanide solution evaporating and crystallizing the solution. Cobaltocyanide of potassium is first formed, which is subsequently decomposed into cobalticyanide on heating, with evolution of hydrogen; any carbonate or excess potassium cyanide that may be present is decomposed by the addition of acetic acid, and the potassium cobalticyanide precipitated by alcohol.

Most of the soluble cobalticyanides can be readily obtained from the barium salt by double decomposition with the corresponding sulphates, and the barium salt is best prepared by saturating a mixture of barium carbonate and cobalt sulphate with hydrocyanic acid and boiling the filtered solution; or by adding cobalt sulphate to a solution of barium cyanide so long as the cobalt cyanide is dissolved, then boiling the solution and crystallizing the barium cobalticyanide.

[1] Descamps, *Ann. Chem. Phys.* [5], **27**, 178.

The cobalticyanides are remarkably stable compounds; the hydrocobalticyanic acid may be boiled with water or strong nitric, or hydrochloric acid without decomposition, and it is only slowly attacked with sulphuric acid. The aqueous solution has strongly acid properties readily neutralizing the carbonates of the alkalis with evolution of carbon dioxide, and attacking zinc and iron with liberation of hydrogen.

The cobalticyanides of the alkali and alkaline earth metals are all soluble in water, and form crystals of a very pale yellow colour. No precipitate is formed when a solution of a ferric, mercuric, or lead salt is added to a solution of a cobalticyanide; the remaining common heavy metal salts yield precipitates, which are insoluble in water, but none of these precipitates are of a very striking or characteristic colour.

When ignited with concentrated sulphuric acid, all the cobalticyanides are decomposed with evolution of carbon dioxide, and monoxide, and sulphur dioxide, leaving a residue of the sulphates of ammonium and cobalt and the base of the cobalticyanide.

Unlike the iron cyanogen compounds, the cobalticyanides are not decomposed by boiling them with mercuric oxide.

METALLIC COBALTICYANIDES

The ammonium salt, $(NH_4)_3Co(CN)_6H_2O$, is obtained in light yellow crystals very soluble in water. The barium salt, $Ba_3[Co(CN)_6]_22H_2O$, separates in very faint yellow prisms, and is very soluble in water. The double salts $BaKCo(CN)_6 11H_2O$ and $Ba_3[Co(CN)_6]_2$-$BaCl_2 16H_2O$ have been described: Cadmium cobalticyanide, $2Cd_3[Co(CN)_6]_2 15H_2O$, is obtained by double decomposition as a white amorphous powder;[1] as is also the bismuth salt, $Bi[Co(CN)]_0 5H_2O$.

Cobaltous cobalticyanide $Co_3[Co(CN)_6]_2 14H_2O$, is a light red precipitate which dehydrates and turns blue on warming and is insoluble in water. This

[1] S. Fisher and Cuntze, *Chem. Zeit.* (1902), **26**, 892–93.

compound corresponds to the precipitate obtained by the addition of a ferrous salt to a ferricyanide; it combines with ammonia forming the compounds $Co_3[Co(CN)_6]_25NH_3 1\frac{1}{2}H_2O$ and $Co_3[Co(CN)_6]_26NH_3$-$\frac{1}{2}H_2O$. The cupric salt is obtained as a light blue precipitate, insoluble in water or acids, but completely soluble in ammonia, forming a blue solution which yields by evaporation the compound $Cu_3[Co(CN)_6]$-$4NH_3 10H_2O$ in deep blue crystals, insoluble in water. The ferrous salt is obtained as a white precipitate, and the lead salt, $Pb_3[Co(CN)_6]_27H_2O$, crystallizes in scales and is very soluble in water; it forms the basic salts, $Pb_3[Co(CN)_6]_26PbO3H_2O$ and $Pb_3[Co(CN)_6]_2$-$3PbO.14H_2O$; it is also said to form the double salt, $PbKCo(CN)_63H_2O$. The manganous salt is white and insoluble. Mercuric salts form no precipitate, but mercurous salts throw down a white precipitate from a soluble cobalticyanide of the mercurous compound which is quite insoluble in water, and when dried and ignited leaves a residue of cobaltosocobaltic oxide, Co_3O_4, and thus affords an excellent method of estimating cobalticyanides. The nickel compound, $Ni_3[Co(CN)_6]_212H_2O$, is a light blue precipitate insoluble in water. Potassium cobalticyanide, $K_3Co(CN)_6$, which crystallizes in very light yellow prism, is very soluble in water, and is isomorphous with potassium ferricyanide. Silver salts precipitate a white curdy compound, $Ag_3Co(CN)_6$, which when air-dried is anhydrous: it is soluble in ammonia solution, from which it may be separated combined with ammonia. Sodium cobalti-cyanide, $Na_3Co(CN)_62H_2O$, forms large colourless crystals very soluble in hot water. The zinc salt, $Zn_3[Co(CN)_6]_212H_2O$, is white and insoluble, as is also the stannous compound.

A very large number of double salts are also known, and are said to crystallize exceedingly well in large and well-developed crystals.

The strontium salt, $Sr_3[Co(CN)_6]_220H_2O$, is said to form the double salts $SrNH_4Co(CN]_410H_2O$ and $SrKCo(CN)_69H_2O$.

Double salts of cadmium and zinc may be prepared by heating a salt of either of these metals under pressure to 160° C. with an alkaline cobalticyanide. In this manner the compounds $CdKCo(CN)_6$, $CdNaCo(CN)_6H_2O$, in quadratic leaflets; and $ZnKCo(CN)_63H_2O$, quadratic leaflets, and $ZnNaCo(CN)_6H_2O$ in quadratic plates, have been prepared.[1]

Addition compounds with ammonia have also been described,[2] prepared by dissolving the salt in ammonia and precipitating with alcohol, in this manner the salts: $Cd_3[Co(CN)_6]_24NH_3.2H_2O$; $Cd_3[CO(CN)_6]_29NH_32H_{20}$; $Cd_3[Co(CN)_6]_27H_2O$; $Cd_3[Co(CN)_6]_25NH_33H_2O$; $Zn_3[Co(CN)_6]_210NH_39H_2O$; $Zn_3[Co(CN)_6]_26NH_3$ have been obtained.

THE CYANIDES OF COPPER—CUPRIC CYANIDE. The addition of a pure solution of a soluble cyanide to a cupric salt causes the formation of a yellow precipitate which is very probably cupric cyanide, but it is very unstable and rapidly gives off cyanogen even at the ordinary temperature, and is converted into the cuprocupric cyanide, $(CuCN)_2Cu(CN)_25H_2O$. This latter compound may also be obtained by precipitating a solution of a cuprocyanide with a cupric salt. The composition of the precipitate produced by the latter method would, of course, depend upon the particular class of cuprocyanide used. It is obtained of a green colour and is decomposed by acids into cuprous cyanide, hydrocyanic acid, and a cupric salt. With alkalis a double cuprocyanide and cupric oxide are obtained.

Cuprocupric compounds of the composition, $Cu(CN)_2(CuCn)_2H_2O$; $Cu(CN)_2(CuCN)_4H_2O$ have been described by Dufau.[3]

CUPROUS CYANIDE, CuCN, is obtained as a white clotty precipitate by the addition of a solution of an alkaline cyanide or hydrocyanic acid to a solution of cuprous chloride in hydrochloric acid, or a solution of cupric sulphate saturated with sulphur dioxide. It

[1] S. Fisher and A. Cuntze, *Chem. Zeit.* (1902), **26**, 872–73.
[2] Fisher and Cuntze, *l.c.* [3] *Compt. rend.* **36**, 1099.

may also be prepared by adding a dilute mineral acid to a solution of a cuprocyanide.

If the double lead cuprocyanide is suspended in water and decomposed by hydrogen sulphide, cuprous cyanide may be obtained in shining crystals by gently evaporating the filtered solution ; and it may also be formed by warming the precipitated cupric cyanide obtained by adding a cupric salt to a cyanide solution. The compound is first decomposed into cuprocupric cyanide and then into cuprous cyanide thus :

(1) $3Cu(CN)_2 = Cu(CN)_2(CuCN)_2 + (CN)_2$.
(2) $2Cu(CN)_2(CuCN)_2 = 6CuCN + (CN)_2$.

Cuprous cyanide is a white insoluble compound. It is not acted upon by hydrogen sulphide, and is hardly affected by boiling dilute sulphuric acid if chlorides are absent ; but is decomposed by this acid in the presence of chlorides, or by boiling with dilute hydrochloric acid, with evolution of hydrocyanic acid and formation of cuprous chloride. It is slightly soluble in dilute ammonia, in dilute acids, and in ammonium salts, and is completely decomposed by nitric acid. It dissolves in a solution of potassium thiocyanate and forms the salt $2CuCN3KCNS$, which crystallizes in rhombic plates. The compound $2CuCN3NH_4CNS$ is also formed when ammonium thiocyanate is substituted for the potassium salt.[1]

Cuprous cyanide readily dissolves in the solutions of the alkaline cyanides, with which it forms a number of crystalline double salts usually called cuprocyanides, thus : the ammonium salt $NH_4Cu(CN)_2$ crystallizes in colourless crystals which are sparingly soluble in water ; it readily gives off ammonium cyanide when heated, and ultimately leaves pure cuprous cyanide. The barium salt $BaCu_2(CN)_4H_2O$ is obtained by dissolving cuprous cyanide in barium cyanide solution.[2] The calcium salt $CaCu_2(Cn)_45H_2O$, prepared in the same manner, crystallizes in colourless needles and is very

[1] H. Grossmann, *Zeit. anorg. Chem.* (1913), **27**, 407–10.
[2] Miellet, *J. Pharm. Chim.* [3], 3, 413.

soluble in water. Three molecules of water are given off at 100° C. The cadmium salt has the composition $CdCu_2(CN)_4$.[1]

According to Rammelsberg the potassium cuprocyanides may be divided into three classes represented by the formulæ $KCu_2(CN)_3H_2O$; $K_2Cu_2(CN)_4$; $K_6Cu_2(CN)_8$. The compound $KCu_2(CN)_3H_2O$ [2] may be obtained by boiling cuprous thiocyanate with potassium cyanide solution and filtering, when the salt above mentioned crystallizes out; the compound cannot be prepared directly from cuprous cyanide and potassium cyanide. If the mother liquor is concentrated, crystals may be obtained of the composition $2KCN(CuCN)_2 = KCu(CN)_2$ and $4KCN(CuCN)_2$-$2KCNSH_2O$. This latter salt corresponds to the compound of the type $(CuCn)_26KCN$ ($= K_6Cu_2(Cn)_8$ or $K_3Cu(Cn)_4$) with two molecules of thiocyanate in place of two molecules of potassium cyanide. This body is very soluble in water and is said to give characteristic reactions with copper and mercuric salts.

The compound $2KCN(CuCN)_2$ or $KCu(CN)_2$ may also be prepared by precipitating the calcium salt with potassium carbonate or by dissolving cuprous cyanide in potassium cyanide solution. It is moderately soluble in water and crystallizes in colourless anhydrous crystals.

Sodium cuprocyanide may be prepared by dissolving cuprous cyanide in sodium cyanide solution. It crystallizes in white needles moderately soluble in water of the composition $Na_2Cu(CN)_33H_2O$.

A large number of compounds of the copper cyanides and ammonia have been described. When cuprous cyanide is dissolved in aqueous ammonia and the colourless solution exposed to the air, oxygen is absorbed, and the solution turns blue. If then evaporated but keeping the liquid ammoniacal, beautiful green prismatic needles with a metallic lustre are obtained of ammoniacal cuprosocupric cyanide,

[1] Schuler, *A.*, 87, 46.

[2] Ilzog, *Ber.*, 35 [i], 106–10; *J.S.C.I.*, 21, 286.

$Cu'_2Cu''(CN)_4 4NH_3$. This compound is soluble in ammonia, but insoluble in water, and is unaltered by the air. A compound in deep blue crystals containing a larger proportion of ammonia may be obtained by dissolving the above compound in warm ammonia liquor, and passing ammonia gas in. On exposure to the air it yields up ammonia and passes into the green compound.

By adding manganese acetate to a solution of potassium cuprocyanide, $K_3Cu(Cn)_4$, crystals of potassium cupromanganocyanide may be obtained [1] in white cubes which are stable only in the wet state, and are readily oxidized. They are insoluble in water and may be completely decomposed by boiling with alkaline carbonate or hydroxide.

The sodium salt which may be obtained in a similar manner is said to be more stable, and crystallizes in six-sided prisms.

THE CYANIDES OF GOLD—AURIC CYANIDE. This body has never been prepared in a free state; the product obtained by acidifying a solution of potassium auric cyanide is hydrogen aurocyanide. Potassium auricyanide, $KAu(CN)_4 1\frac{1}{2}H_2O$, may be prepared by adding neutral auric chloride to a hot and concentrated solution of potassium cyanide. On cooling the liquid colourless tablets of the potassium double salt separate out. The salt is very soluble in water, but is insoluble in alcohol. The hydrogen salt $HAu(CN)_4 3H_2O$ is best prepared by decomposing the silver salt with the equivalent quantity of hydrochloric acid, or the barium salt with sulphuric acid, and can be crystallized in white tablets soluble in water, alcohol, and ether. When the solution is boiled, hydrocyanic acid is evolved and aurous cyanide precipitated. The crystals on ignition evolve hydrocyanic acid and cyanogen, and leave a residue of metallic gold.

AUROUS CYANIDE may be isolated from potassium aurocyanate if a solution of this salt is boiled with

[1] P. Straus, *Zeit. anorg. Chem.* (1895), 9, 6–18.

hydrochloric acid, when hydrocyanic acid is evolved and a yellow crystalline precipitate of aurous cyanide formed.

Aurous cyanide is insoluble in water, alcohol and ether. When heated in the dry state it behaves like the cyanides of the other noble metals, cyanogen gas is evolved and a residue of metallic gold and some paracyanogen left. It is soluble in a solution of potassium cyanide, ammonia or a thiosulphate. It is not acted on by boiling aqueous hydrochloric, nitric or sulphuric acids, or by hydrogen sulphide. It is, however, completely decomposed by ammonium sulphide forming aurous sulphide. It is soluble in hot caustic alkaline solutions forming double aurocyanides and precipitating metallic gold, and it is also readily soluble in alkaline cyanide solutions.

When aurous cyanide is heated with a solution of potassium ferrocyanide and oxygen passed through potassium, aurocyanide is formed :

$$8AuCN + 2K_4Fe(CN)_6 + 5H_2O + O = 8KAu(CN)_2 + 2Fe(OH)_3 + 4HCN.$$

Gold hydroxide is said to act in a similar manner.[1]

POTASSIUM AUROCYANIDE, $AuK(CN)_2$, is obtained by dissolving aurous cyanide, oxide, or metallic gold in potassium cyanide solution, in the latter case in the presence of oxygen. By evaporating and cooling the solution the double salt may be obtained in colourless crystals which are soluble in water, sparingly soluble in alcohol, and insoluble in ether.

By treating the solution with iodine and cooling, dark brown violet crystals, having the composition $KAu(CN)_2I_2$, may be obtained. Similar compounds may also be prepared by treating the salt with chlorine or bromine. This reaction is a general one for the soluble double aurocyanides. The additive compounds

[1] Ernst Beutel *Monatsch* (1910), **31**, 883–86; *J.C.S.* (1910), i. 723.

with chlorine are generally colourless, and with bromine yellow.

The aqueous solutions of the alkali metal aurocyanides are used in electroplating.

A number of aurocyanides have been prepared, such as the ammonium salt $NH_4Au(CN)_2$; the barium salt $Ba(Au(CN)_2)_2 2H_2O$; the calcium salts $Ca(Au(CN)_2)_2 \cdot 3H_2O$; the cadmium salt $Cd(Au(CN)_2)_2$; and the sodium compound $NaAu(CN)_2$.

HYDROCYANIC ACID (prussic acid; Ger. Blausäure), HCN.

This compound occurs in nature in combination as the glucoside, amygdalin obtained from the bitter almond, and cherry kernels, etc. The compound is also found in combination in certain other glucosides.

When bitter almonds are ground up and kept in contact with water, fermentation sets in with decomposition of the amygdalin due to the action of the enzyme emulsin thus:

$$C_{20}H_{27}NO_{11} + 2H_2O = C_7H_6O + HCN + 2C_6H_{12}O_6,$$

benzaldehyde, glucose and hydrocyanic acid being formed.

This acid was first discovered by Scheel in 1782, who showed that the blue forming properties of the melt obtained in the fusion of dried blood and potash was lost by acidifying and boiling the solution, but could be recovered from the vapours. He also obtained the compound by distilling a ferrocyanide with an acid, and showed that it was inflammable, and that its combustion products were carbon dioxide and nitrogen. But it was not until a little over thirty years after that Gay Lussac [1] published the exact quantitative composition.

Hydrocyanic acid is best obtained in aqueous solution by distilling an alkaline cyanide solution with a dilute acid, or by distilling potassium or sodium ferrocyanide solution with dilute sulphuric acid with or without the addition of cuprous chloride.

[1] *Annalen* (1815), **95**, 156.

Without the addition of a small quantity of cuprous chloride only 50 per cent. of the total cyanogen is obtained as hydrocyanic acid thus :

$$2K_4Fe(CN)_6 + 3H_2SO_4 = 6HCN + Fe''K_2Fe(CN)_6 + 3K_2SO_4.$$

With cuprous chloride addition complete decomposition occurs thus :

$$K_4Fe(CN)_6 + 3H_2SO_4 = 6HCN + FeSO_4 + 2K_2SO_4.$$

The acid may also be prepared :

By heating ammonium formate to 200° C. :

$$NH_4CHO_2 = HCN + 2H_2O.$$

By passing electric sparks through an atmosphere of acetylene and nitrogen :

$$C_2H_2 + N_2 = 2HCN.$$

By the action of chloroform on ammonia, when the vapours are passed through a red-hot tube :

$$CCl_3H + NH_3 = HCN + 3HCl.$$

By the action of nitric acid on certain phenols :

And by many other methods. It is also said to occur to a limited extent in tobacco smoke.

The pure anhydrous acid is prepared by passing pure dry hydrogen sulphide through a tube containing dry mercuric cyanide :

$$Hg(CN)_2 + H_2S = HgS + 2HCN.$$

Any excess hydrogen sulphide is usually removed by passing the gases through some lead carbonate, but a better arrangement is to have a second tube packed with pure dry mercuric cyanide, and to stop the passage of the hydrogen sulphide when the mercury cyanide in the second tube shows signs of turning black ; the anhydrous acid is passed into a receiver cooled by freezing mixture and condensed.

This acid is an intense poison, and its preparation should not be lightly undertaken, but prepared only when necessary, the operation being performed under a well-ventilated hood, or in the open air, for to inhale the vapour of the pure acid would be instantly fatal.

The preparation of the aqueous solution should also be performed with caution. Inhalation of small traces of this gas for any length of time is liable to give rise to nervous depression in the operator, accompanied by intense headache.

Hydrocyanic acid is an endothermic compound, its heat of formation being – 27 480. The specific gravity of the anhydrous acid at 7° C. = 0.705, and 0.6967 at 18° C.;[1] it solidifies at – 15° C.; and boils at 26.5° C. at 760 mm. pressure.

It is inflammable and gives out 158620 heat units on complete combustion, forming carbon dioxide, nitrogen and water vapour. It is miscible with water, ether and alcohol in all proportions.

The acid combines with the alkali and alkaline earth metal hydroxides, but has no action on their carbonates. With mercuric oxide it combines with energy to form mercuric cyanide; it is decomposed by strong hydrochloric or sulphuric acid, especially on heating to form ammonium formate.

The solution of the acid may be kept for some time without alteration if pure, but with a trace of alkaline cyanide the acid rapidly decomposes, the colour changing to dark brown, and it finally deposits dark brown flocks of azulmic acid, and other decomposition products are left in solution. This action may be prevented by the addition of a small quantity of a mineral acid, and it may also be kept for some time without decomposition, by the addition of 20 per cent. of glycerine.[2]

Aqueous hydrocyanic acid when treated with hydrogen peroxide gradually changes to a crystalline precipitate of oxamide:

$$2HCN + H_2O_2 = C_2H_4N_2O_2.$$

And unlike the alkaline cyanides the aqueous acid does not yield the red-coloured reaction with picric acid.

[1] Gay Lussac. [2] J. Williams.

INDIUM CYANIDE is very unstable. The precipitate which forms when a soluble cyanide is added to a solution of an indium salt dissolves in excess of the cyanide, but it is decomposed on heating, indium hydroxide being precipitated with evolution of oxygen.[1]

IRIDIUM CYANIDE, $Ir(CN)_3$, forms a series of double salts known as iridocyanides. The simple cyanide is best prepared by boiling the hydroiridiocyanic acid with hydrochloric acid, and is obtained as a green powder. These compounds have been studied by Martius ;[2] Claus ;[3] Wohler and Booth ;[4] and Rammelsburg.[5]

The potassium double salt $K_3Ir(CN)_6$ is obtained by fusing iridium ammonium chloride with potassium cyanide ; the double cyanide is dissolved out of the melt with water and crystallized.

The salt crystallizes in colourless orthorhombic prisms, which are anhydrous. It is exceedingly stable but is insoluble in alcohol. The barium salt $Ba_3[Ir(CN)_6]_2 18H_2O$, prepared by boiling the light blue precipitate of iridiocyanide of copper with barium hydroxide, is also stable.

Hydroiridiocyanic acid is easily prepared from the barium salt by adding the theoretical quantity of dilute sulphuric acid. It is a strong acid which is very soluble in water and alcohol and may be obtained in crystals.

THE CYANIDES OF IRON—FERRIC CYANIDE. No simple ferric cyanide has as yet been obtained, for when a ferric salt solution is added to an alkaline cyanide solution, a reddish brown precipitate is immediately formed which consists wholly of ferric hydroxide, the solution containing free hydrocyanic acid :

$$6KCN + 2FeCl_3 + 6H_2O = 6KCl + 6HCN + Fe_2(OH)_6.$$

Nor do simple double ferric cyanides appear to exist, for when a ferric salt is added to a solution of a simple double cyanide such as the sodium or potassium nickel

[1] Meyer, *J.* (1865), 244. [2] *A.*, **117**, 357.
[3] *J.* (1855), 444. [4] *P.*, **31**, 161. [5] *P.*, **42**, 140.

cyanide, a precipitate occurs after a few seconds of a mixture of ferric hydroxide and nickel cyanide :

$$3K_2Ni(CN)_4 + 2FeCl_3 + 6H_2O = 6KCl + 3Ni(CN)_2 + 6HCN + Fe_2(OH)_6.$$

A similar action takes place if the double zinc cyanide is substituted for the nickel salt.

FERROUS CYANIDE. When potassium cyanide solution is added to a solution of ferrous sulphate, the latter being kept in excess, a fine orange-coloured precipitate is obtained. This compound is, however, not pure ferrous cyanide, one-fifth of the total cyanogen being combined with potassium thus : $KFe_2''(CN)_5$ or $KCN : 2Fe''(CN)_2$. If the ferrous salt is precipitated with sodium cyanide solution a double ferrous sodium cyanide is produced, but containing a smaller proportion of alkali metal than the compound described above, only one-ninth of the total cyanogen being combined with the alkali metal, thus: $NaFe_4''(CN)_9$ or $NaCN + 4Fe''(CN)_2$. With ammonium cyanide solution or sodium cyanide to which a large quantity of ammonium chloride has been added, an orange. precipitate is obtained of the composition $NH_4Fe''(CN)_3$.

If, however, ferrous chloride solution is precipitated with a solution of freshly prepared calcium cyanide an orange red precipitate is obtained of the pure simple ferrous cyanide of the formula $Fe''(CN)_2$.

These orange-coloured ferrous cyanides form a series thus :

Name.	Formula.	Ratio Fe : CN.
Ammonium ferrous cyanide	$NH_4Fe(CN)_3 = NH_4CN : Fe(CN)_2$	1 : 3
Potassium ferrous cyanide	$KFe_2(CN)_5 = KCN : 2Fe(CN)_2$	2 : 5
Sodium ferrous cyanide	$NaFe_4(CN)_9 = NaCN : 4Fe(CN)_2$	4 : 9
Ferrous cyanide	$Fe(CN)_2$	1 : 2

These compounds are all soluble in excess of the alkaline cyanide solution with formation of a ferrocyanide, and oxidize on exposure to the air with

formation of blue compounds. Oxidizing agents such as ferric chloride or nitric acid also produce blue compounds, which, however, differ from the blue ferric ferrocyanide both in physical appearance and in chemical properties, the colour being lighter and quite devoid of bronze lustre, and when decomposed by alkaline hydroxide solutions in the cold, ferric hydroxide is precipitated and an orange-red solution obtained, which on warming deposits a considerable amount of either ferric hydroxide or black ferrosoferric hydroxide, with formation of a ferrocyanide in solution.[1]

White ferrous ferrocyanide obtained by precipitating calcium or hydrogen ferrocyanide with a ferrous salt, or by distilling these ferrocyanides with a dilute mineral acid, may be considered as a polymeric modification of ferrous cyanide, thus ferrous ferrocyanide: $Fe_2''Fe(CN)_6 = 3[Fe(CN)_2]$. The compound, however, is not a simple cyanide, one of the three atoms of iron being very strongly combined with the cyanogen to form the complex radicle ferrocyanogen, $^{iv}Fe(CN)_6$.

As the complex iron cyanogen compounds occur in such large numbers, many of which are of great interest and importance, they have been considered separately under the heading of "iron cyanogen compounds" (chap. iv and v).

LANTHIUM CYANIDE is formed as a gelatinous precipitate when potassium cyanide is added to a lanthanium salt.

LITHIUM CYANIDE, LiCN, may be obtained by passing hydrocyanic acid into lithium hydroxide solution; it may also be made together with cyanamide by passing nitrogen over heated lithium carbide.

LEAD CYANIDE is obtained by direct precipitation as a basic salt which varies in composition according to the concentration of the solution used, the more dilute the solution the more basic the precipitate. The compound $Pb(CN)_2 2PbO$ may be prepared by adding

[1] H. E. Williams, *Chem. World.* 3, 164.

a cyanide solution to an ammoniacal solution of lead acetate as a white precipitate.[1]

If the oxycyanide is boiled under a condenser with a 5 per cent. solution of hydrocyanic acid and the solution filtered and evaporated in a vacuum, pure lead cyanide may be obtained in the form of yellow needles. These crystals are unattacked by concentrated sulphuric or nitric acid in the cold, but converted by water into the oxycyanide.[2]

Several insoluble double cyanides of lead are known. According to Rammelsberg, potassium zinc cyanide precipitated by lead acetate forms the compound $PbZn(CN)_4$; when a double nickel cyanide is precipitated in a similar manner, however, the basic compound $PbNi(CN)_4PbO2H_2O$ is obtained as a dense granular yellow compound.

MAGNESIUM CYANIDE, $Mg(CN)_2$, is very unstable, and is known only in solution. It may be prepared by adding magnesium sulphate to a solution of barium cyanide. Like the calcium salt the solution is completely decomposed on boiling, the whole of the cyanogen being evolved as hydrocyanic acid, with precipitation of magnesium hydroxide :

$$Mg(CN)_2 + 2H_2O = 2HCN + Mg(OH)_2.$$

Some simple double magnesium cyanides are known and may be obtained in crystals, *e.g.* $MgNi(CN)_4$-$7H_2O$.[3]

MANGANESE CYANIDE. No simple cyanide of manganese has as yet been isolated; but two series of double cyanides are known, similar to the ferrocyanides and ferricyanides. By adding solid potassium cyanide to a solution of manganese acetate, potassium manganocyanide, $K_4Mn(CN)_63H_2O$, is formed, from which crystals of a deep violet colour may be separated.

It may be prepared by P. Straus' modification of Christensen's method,[4] 15 grm. of manganese acetate

[1] Erlenmeyer, *J. für Chem.*, **48**, 356.
[2] M. M. Gupta, *P.C.S.* (1913), No. 324.
[3] H. E. W. [4] *Z. anorg. Chem.* (1895), **9**, 6–18.

are dissolved in 90 c.c. of cold water, and then added to 50 c.c. of a solution containing 25 grm. of potassium cyanide; a green precipitate is obtained which is redissolved by heating on the water-bath with the addition of a further 25 grm. of potassium cyanide. Dark violet crystals of potassium manganocyanide crystallize out on cooling the solution. The sodium salt $Na_4Mn(CN)_6 8H_2O$ and the barium salt $Ba_2Mn(CN)_6$ may be prepared in a similar manner tc the potassium salt, but the calcium salt $Ca_2Mn(CN)_6$ is obtained by precipitation when alcohol is added to the mixed solutions of calcium cyanide and manganese acetate. These salts are readily oxidized in the air to the manganicyanides.

POTASSIUM MANGANICYANIDE, $K_3Mn(CN)_6$, is formed by exposing a solution of the manganocyanide to the air, or by heating, and may be obtained in the form of red-brown needles which are very unstable. The aqueous solution becomes turbid on keeping, and deposits black manganese hydrate. The salt is also readily decomposed by acids and the greater part of the manganese may be precipitated by ammonium sulphide. When a solution of the potassium salt is added to a ferrous salt a dark blue precipitate is obtained; with zinc and cadmium, rose coloured; with lead salts brown, and silver yellowish brown, which turns scarlet in presence of free acid.

The following method for the preparation of the potassium salt has been described by J. Meyer:[1] 400 grm. of potassium cyanide are dissolved in the smallest possible quantity of water, 100 grm. of powdered manganese carbonate added, and air bubbled through the mixture. At first a blue mass of manganocyanide is formed which gradually changes colour to orange-red. It is then gently warmed on the water-bath for about one day, and the precipitate washed with alcohol, and ether, and air dried:

$$2K_4Mn(CN)_6 + O + H_2O = 2K_3Mn(CN)_6 + 2KOH.$$

[1] *Z. anorg. Chem.* (1913), **81**, 385.

The compound may be recrystallized from 10 per cent. potassium cyanide solution. It is decomposed by boiling with water with evolution of hydrocyanic acid, and precipitation of manganese hydroxide. The corresponding sodium salt $Na_3Mn(CN)_6 8H_2O$ may be prepared in a similar manner.

MERCURIC CYANIDE, $Hg(CN)_2$, is one of the most stable of the simple cyanides, and is formed when any simple cyanide is heated with mercuric oxide or a mercuric salt, or by heating a ferrocyanide in a similar manner :

$$2KCN + HgCl_2 = Hg(CN)_2 + 2KCl.$$
$$2KCN + H_2O + HgO = Hg(CN)_2 + 2KOH.$$
$$4H_2O + 2K_4Fe(CN)_6 + 7HgO = 8KOH + Fe_2O_3 + 6Hg(CN)_2 + Hg.$$

It may also be obtained by the direct action of hydrocyanic acid on mercuric oxide, combination taking place with evolution of energy. The cyanide may be recovered by evaporating the solution in colourless, transparent, and anhydrous crystals, very permanent in the air and intensely poisonous.

The compound may be conveniently prepared by the method described by E. Rupp and S. Goy :[1] 31 grm. of sodium cyanide in powder form are mixed with 50 c.c. of water and added gradually with stirring to 90 grm of mercuric sulphate. The mixture evolves considerable heat. If the colour is yellow, due to the presence of some basic mercuric sulphate, a little more sodium cyanide must be added.

The cooled solid mass is ground and treated in an extraction apparatus with 95 per cent. alcohol, and the mercuric cyanide purified by recrystallization from water after removal of the alcohol.

The salt dissolves in eight parts of cold water, and is soluble in alcohol. It possesses great stability and is unchanged by boiling with water, even in the presence of caustic alkali, but is completely decomposed by strong sulphuric acid. In aqueous solutions it is decomposed by hydrochloric, hydrobromic, hydriodic

[1] *Apoth. Zeit.* (1908), **23**, 374.

acids or hydrogen sulphide, with liberation of hydrocyanic acid. The reaction with hydrochloric acid, however, is only complete in the presence of ammonium chloride. A mixture of sodium chloride and oxalic acid [1] or tartaric acid and ammonium chloride [2] has been suggested in place of the hydrochloric acid, in order to obtain complete decomposition of the mercuric cyanide. When the salt is heated with dry ammonium chloride, ammonium cyanide is evolved; and when the aqueous solution is treated with a polysulphide, mercuric sulphide is precipitated and a thiocyanate is formed in solution. Hydrogen sulphide completely removes the mercury from the compound, either in the dry state, or from its solution in water or alcohol.

A warm aqueous solution of mercuric cyanide dissolves a considerable quantity of mercuric oxide, and on cooling the solution needles of mercuric oxycyanide, $Hg(CN)_2HgO$, are deposited, which are sparingly soluble in cold water.

Mercuric oxycyanide may be easily prepared in almost theoretical yield by dissolving 52 grm. of mercuric cyanide and 50 grm. of mercuric chloride in 300 c.c. of warm water. A solution of 15 to 30 per cent. sodium hydroxide is then gradually added with frequent agitation until the precipitate is pure white in colour. The mixture is allowed to stand twenty-four hours and then filtered and washed.[3] It may also be prepared directly from sodium cyanide, by adding 360 grm. of powdered mercuric chloride to a solution of 70 grm. of sodium cyanide in 350 to 500 c.c. of water. The solution is filtered, if necessary, and then a solution of 25 per cent. sodium hydroxide gradually added with agitation until the precipitate is free from colour; the mixture is left to stand for one day and then filtered and thoroughly washed.[4]

By the addition of various acids to the mercuric oxycyanide in quantities sufficient to neutralize the

[1] P. Pugge. [2] Lops, *J.C.S.* (1893), ii. 502.
[3] E. Rupp and S. Goy, *Arch. Pharm.*, **246**, 367–73.
[4] Rupp and Goy, *l.c.*

free mercuric oxide, E. Rupp and Goy[1] have obtained a number of crystalline double salts, such, for example, as the mercuric cyanide nitrate, $Hg(CN)_2Hg(NO_3)_2$, in colourless plates; double cyanide acetate, $Hg(CN)_2Hg(C_2H_3O_2)_2$, in slender needles; cyanide formate, $Hg(CN)_2Hg(HCO_2)_2$, in prisms; the oxalate, $Hg(CN)_2HgC_2O_4$, as a crystalline powder; cyanide succinate, $Hg(CN)_2HgC_4H_4O_4 2H_2O$, in long prisms; cyanide benzoate, $Hg(CN)_2Hg(C_7H_5O_2)_2H_2O$, in long prisms decomposed by water. The same investigators have shown that when the oxycyanide is treated with hydrochloric or hydrobromic acid, mercuric cyanide chloride and mercuric cyanide bromide are formed respectively, but when the oxycyanide is treated with hydriodic acid the behaviour is quite different, the mercuric cyanide being completely decomposed, forming mercuric iodide and free hydrocyanic acid.

On adding potassium iodide solution to a cold saturated solution of mercuric oxycyanide a pale red precipitate of glittering crystals is formed, which dissolves in excess of the potassium iodide. This reaction occurs in two stages;[2] with moderate amounts of potassium iodide the complex compound $Hg(CN)_2$-$HgI_2 2KCN$ is formed, which is decomposed on acidification with precipitation of mercuric iodide; with an excess of the iodide the whole of mercuric cyanide is changed into the double potassic mercuric iodide K_2HgI_4, and no precipitate is formed on acidification. On concentrating the solution, however, the triple salt separates: this salt has an alkaline reaction, and yields half its cyanogen on acidification.

If mercuric cyanide is dissolved to saturation in strong ammonia by gentle heating, long crystals of the ammonia compound $Hg(CN)_2NH_3$ separate out on cooling, which may be dried unchanged in an atmosphere of ammonia, but which lose all the ammonia on exposure to the air. It is but slightly soluble in water.[3]

[1] *Arch. Pharm.* (1912), **250**, 280–90.
[2] Rupp and Goy, *l.c.* [3] *J.S.C.I.*, **13**, 548.

When potassium cyanide is added to a solution containing mercuric chloride and potassium thiocyanate or potassium mercuric thiocyanate, brilliant glistening needles separate out of the salt $Hg(CN)_2$-$2KCN{\cdot}KCNS\frac{1}{2}H_2O$, mercuric potassium cyanothiocyanate.[1]

A large number of double mercuric cyanides are known. They may be prepared by crystallizing the two cyanides together, or by adding a solution of a salt of the metal to the double potassium salt if the compound is insoluble. A double zinc salt is used in pharmacy, known as Lister's antiseptic. It has been shown to be trizincic, monomercuric octocyanide, $Zn_3Hg(CN)_8$;[2] the compound is obtained as a white precipitate by adding a zinc salt to potassium mercuric cyanide. The lead compound is also obtained as a white precipitate. Potassium mercuric cyanide, $K_2Hg(CN)_4$, crystallizes in regular octahedra which are permanent in the air. The sodium salt also crystallizes in octahedra. The compounds $3Hg(CN)_2{\cdot}2Cd(CN)_2$,[3] $Hg(CN)_2HgO.7AgCN$,[4] $Hg(CN)_2N(CH_3)_4CN$[5] have been prepared. $BaHg(CN)_4{\cdot}3H_2O$ and $SrHg(CN)_4{\cdot}5H_2O$, which crystallize in needles; $CaHg_2(CN)_6{\cdot}3H_2O$, in colourless hydroscopic needles; $Ca_2Hg_3(CN)_{10}{\cdot}6H_2O$, in six-sided prisms, and $Mg_2Hg_3(CN)_{10}{\cdot}5H_2O$, have been described by Grossman and P. von der Forst.[6]

Mercuric cyanide possesses the property of forming crystalline compounds with many salts. A very great number of these double salts have been prepared and recorded by different investigators, and the following are a few typical examples.

With metallic chlorides, compounds of the type $Hg(CN)_2MCl$, $Hg(CN)_2M''Cl_2$ and $2Hg(CN)_2M''Cl_2$; with soluble bromides, compounds of the type $Hg(CN)_2MBr$; $2Hg(CN)_2M''Br_2$; with iodides, $Hg(CN)_2KI$; with

[1] H. Grosmann, *Z. anorg. Chem.* (1913), **37**, 407–10; *J.C.S.* (1913), i. 146.

[2] W. R. Dunstan, *P.C.S.* (1908), **24**, 135.

[3] Schuler, *A.*, **87**, 46. [4] Bloxam, *Ber.*, **16**, 2669.

[5] Claus and Merk, *Ber.*, **16**, 2737. [6] *Ber.* (1904), **37**, 4141.

formates, $Hg(CN)_2 2CH(NH_4)O_2 + Hg(CN)_2 2CHKO_2$; with chromates, $2Hg(CN)_2K_2CrO_4$, long light yellow needles; $2Hg(CN)_2Ag_2CrO_4CrO_3$, splendid red needles; the double chlorochromate, $6Hg(CN)_2(NH_4)_6Cr_2O_7Cl_4 4H_2O$, and the chromate, $3Hg(CN)_2 2K_2CrO_4 2H_2O$, have been prepared by D. Stromholm.[1]

MOLYBDENUM CYANIDE. The potassium salt of a double cyanide of molybdenum, in which the molybdenum forms a complex union with the cyanogen, has been prepared and described by Chilesotti,[2] of the formula $K_4Mo(CN)_8 2H_2O$.

A potassium salt of a reddish violet colour had been previously described by Heide and Hofmann,[3] which was said to have the formula $4KCNMoO_2 10H_2O$. These salts become blue on dehydration, and are only prepared in strongly alkaline solutions; the addition of alkaline cyanides converts them into a series of yellow salts of the type $R_4Mo(CN)_8$aq., and the following salts of this series have been described by Rosenheim and Garfunkel.[4] The manganese salt, $Mn_2Mo(CN)_8 8H_2O$, forms light yellow leaflets; the silveramine salt, $[Ag_4(NH_3)_2]Mo(CN)_8$; the nickel-amine, $[Ni(NH_3)_4]_2Mo(CN)_8 8H_2O$; and pyridinium salt, $[C_5NH_6]_4Mo(CN)_8$. The hydrogen salt, $H_4Mo(CN)_8 6H_2O$, is prepared by adding hydrochloric acid to a strong solution of the potassium salt and extracting the acid with alcohol, and the salt separated by placing in a freezing mixture after the addition of ether.

NICKEL CYANIDE, $Ni(CN)_2 7H_2O$, is produced when a solution of an alkaline cyanide is added to an excess of a nickel salt solution, as an apple-green gelatinous precipitate, which when air-dried has the composition expressed above, and at 200° C. becomes anhydrous.

It is readily decomposed by boiling dilute hydrochloric or sulphuric acid, and is readily soluble in aqueous ammonia, which on evaporation deposits a

[1] *Z. anorg. Chem.* (1913), **80**, 155.
[2] *J.C.S.* (1905), i. 177. [3] *J.C.S.* (1896), ii. 605.
[4] *Z. anorg. Chem.* (1909), **65**, 166–77; *J.C.S.* (1910), i. 101 and 232.

micro-crystalline precipitate of an ammoniacal nickel cyanide of a light mauve or lilac colour, having the composition $[Ni(CN)_2]_2 3NH_3 4H_2O$. The same compound is produced by repeatedly evaporating a solution of the double ammonium nickel cyanide :

$$2(NH_4)_2Ni(CN)_4 + 4H_2O = [Ni(CN)_2]_2 3NH_3 4H_2O + 3HCN + NH_4CN.$$

By adding potassium cyanide to a moderately strong solution of a nickel salt followed by excess of ammonia, steel-blue leaflets separate out after some days of the compound, $Ni(CN)_2 4NH_3$; if acetic is carefully added to the solution and then benzene a bluish white precipitate of the composition, $Ni(CN)_2NH_3C_6H_6$, is obtained and no benzene is lost on air-drying. A similar compound may be obtained with aniline, $Ni(CN)_2NH_3NH_2C_6H_5$, as a violet-white precipitate ; and with phenol, $Ni(CN)_2NH_3C_6H_5OH.H_2O$.[1] The hydrazine compound, $Ni(CN)_2(H_2N_4)_2$, has been described.

Nickel cyanide dissolves very readily in a solution of an alkaline cyanide, forming an orange-red solution of a double nickel cyanide of the type, $M'_2Ni(CN)_4$.

The double nickel cyanides of the alkali and alkaline earth metals, including lithium and magnesium, are fairly soluble in water, from which they crystallize in well-formed deep orange-red crystals. The salts are stable in solution and in the solid state, but are completely decomposed by dilute sulphuric or hydrochloric acids. The addition of mercuric chloride to a solution of the salts also decomposes them with formation of mercuric cyanide. No nickel sulphide is precipitated by passing hydrogen sulphide through their solution, or by boiling with alkaline sulphides.

When the soluble double salts are reduced, a red solution is obtained, in which the nickel is said to be univalent.[2]

The double nickel cyanides of barium, calcium, and

[1] K. Hofmann and E. Hochllen, *Ber.* (1903), **36**, 1149 ; *J.C.S.* (1903), i. 469.

[2] J. Bellucci and R. Corelli, *Atti R. Accad. Lincei* (1913) [v] 22, i. 603.

strontium are best prepared by dissolving nickel cyanide in the respective cyanide solutions. The barium salt may also be prepared by passing hydrocyanic acid into water in which nickel sulphate is dissolved, and containing twice the equivalent quantity of barium carbonate in suspension :

$$NiSO_4 + 2BaCO_3 + 4HCN = BaNi(CN)_4 + BaSO_4 + 2CO_2 + 2H_2O.$$

From the barium salt the other soluble double salts may be prepared by precipitation with the corresponding sulphate.

DOUBLE NICKEL CYANIDES. The ammonium salt, $(NH_4)_2Ni(CN)_4H_2O$, forms deep red-brown crystals. The salt is very unstable in solution, and when boiled under atmospheric pressure evolves hydrocyanic acid and ammonium cyanide and depositing the ammoniacal compound, $[Ni(CN)_2]_23NH_34H_2O$. To obtain crystals of the double salt the solution must be evaporated under greatly reduced pressure. The barium salt, $BaNi(CN)_45H_2O$, crystallizes in large, deep orange-red crystals. The calcium salt, $CaNi(CN)_45H_2O$, in deep orange-red prismatic needles, which may be obtained several inches in length ; when heated to 100° C. two molecules of water are lost. The lead salt prepared by precipitating the calcium salt with lead acetate separates as an insoluble dense granular yellow precipitate of a basic compound, of the composition $PbNi(CN)_4PbO2H_2O$. The magnesium salt, $MgNi(CN)_47H_2O$, is a very unstable salt, and its solution rapidly decomposes on boiling under ordinary pressure, but it may be obtained in crystals by evaporating its solution in a vacuum. The potassium salt, $K_2Ni(CN)_4$-H_2O, crystallizes in dense deep orange-yellow crystals, very stable in the solid state and in solution. The sodium salt, $Na_2Ni(CN)_43H_2O$, crystallizes well in small orange-yellow prisms, which become anhydrous when heated to 100° C. The strontium salt, $SrNi(CN)_4$-$5H_2O$, is fairly stable in solution, and loses three molecules of water at 100° C.

A solution of sodium or potassium nickel cyanide forms a white precipitate with ferrous salts of ferrous nickel cyanide from which the double alkali nickel cyanide may be recovered, with precipitation of ferrous hydroxide, by boiling the compound with caustic alkalis, no ferrocyanide being formed; with ferric salts a reddish precipitate of nickel cyanide and ferric hydroxide is obtained, with evolution of hydrocyanic acid; a white precipitate is also obtained with a solution of a cadmium, manganese, or zinc salt. Red silver chromate is not decomposed by a solution of the double salt, and in this fact differs from many of the other simple double cyanides.

OSMIUM CYANIDE, $Os(CN)_2$, is obtained when a solution of an osmiocyanide is boiled with hydrochloric acid. It is the only osmium cyanide known in the free state.

POTASSIUM OSMIOCYANIDE, $K_4Os(CN)_6 3H_2O$, was discovered by Claus, and may be prepared by adding a solution of potassium cyanide to a solution of potassium osmiate. The solution is evaporated to dryness, and gently ignited out of air contact, redissolved in a small quantity of water, filtered and crystallized. The salt is obtained in yellow crystals, which, when heated with strong hydrochloric acid, are converted first into hydrogen osmiocyanide, and then into hydrocyanic acid and osmium dicyanide.

Precipitates are obtained with a solution of this salt and metallic salts somewhat similar to the corresponding ferrocyanides. With ferrous salts a light blue precipitate is obtained, which darkens on oxidation; with ferric salts a deep violet precipitate; the copper salt is brown and insoluble, and the silver, lead, zinc, and cadmium salts are white insoluble precipitates.

The barium salt, $Ba_2Os(CN)_6 3H_2O$, prepared by boiling the violet ferric salt with barium hydroxide, crystallizes in reddish-yellow prisms which become anhydrous at 50 to 60° C.

HYDROSMIOCYANIC ACID is prepared as described above, by the addition of strong hydrochloric

acid to a strong solution of the potassium salt. The precipitated acid is filtered off, washed with hydrochloric acid, and dissolved in alcohol, from which, by the addition of a little ether, it crystallizes in colourless anhydrous crystals.

PALLADIUM CYANIDE, $Pd(CN)_2$, is a slightly yellow insoluble compound, precipitated from a palladious salt by the addition of an alkaline cyanide solution. It is unacted upon by acid or mercuric oxide, but it dissolves in aqueous ammonia, from the solution of which the compound $Pd(CN)_2(NH_3)_2$ may be obtained. It is also soluble in solutions of the alkaline cyanides, forming double salts, of which the following have been prepared: the potassium salt, $K_2Pd(CN)_4 3H_2O$, crystallizes in colourless prisms, which effloresce in air; the sodium salt, $Na_2Pd(CN)_4 3H_2O$; the barium salt, $BaPd(CN)_4$, obtained by decomposing the copper salt with a boiling solution of barium hydroxide; the calcium salt, $CaPd(CN)_4 4H_2O$, and the magnesium salt, $MgPd(CN)_4 4H_2O$, are prepared in a similar manner.

Many of the double palladious cyanides are said to be isomorphous with the platinocyanides, and mixed crystals may be obtained.

PLATINUM CYANIDE, $Pt(CN)_2$, may be obtained as a yellow powder or precipitate by igniting the mercurous or ammonium platinocyanide or by adding strong sulphuric acid to a solution of potassium platinocyanide or hydroplatinocyanic acid.

The compound is quite insoluble in water, acids, and alkalis, but in the precipitated state it dissolves in the solutions of alkaline cyanides.

PLATINOUS CYANIDE is characterized by its extraordinary stability. It is quite unaltered by boiling with the diluted mineral acids, even in the presence of cuprous chloride; and it is unattacked by boiling with either mercuric oxide or chloride, in fact it can be prepared by precipitating a solution of mercuric cyanide by a neutral solution of platinous chloride. The cyanide is soluble in a solution of hydrocyanic acid,

from which it is reprecipitated only by continued boiling. The compound, $Pt(CN)_2(NH_3)_2$, is also known.

The solution of platinous cyanide in the alkaline cyanide solutions forms a series of well-defined, very characteristic salts of great interest.

The platinocyanides of the alkali and the alkaline earth metals are soluble in water and are fluorescent, while the salts of the heavy metals are generally insoluble and non-fluorescent.

The fluorescence of these salts is only exhibited in the solid state and not in solution, a fact first demonstrated by Stokes, and two isomeric modifications of the soluble salts have been shown to exist by L. A. Levy, in which the two forms differ in colour and fluorescence. The remarkable colours displayed by the crystalline salts and the fluorescence shown when under the influence of various forms of radiation, together with the formation of a number of coloured hydrates, are properties peculiar to the platinocyanides.

The different hydrates which these salts are capable of forming exhibit different colour phenomena, but the salts in the anhydrous state generally are devoid of colour, and exhibit no fluorescence. The intensity of the fluorescence is also influenced by other salts in the solution from which the platinocyanide was obtained,[1] different salts added to the solution having different effects.

THE METALLIC PLATINOCYANIDES

AMMONIUM PLATINOCYANIDE, $(NH_4)_2Pt(CN)_4H_2O$, may be prepared by dissolving platinous cyanide in ammonium cyanide solutions or by double decomposition between the barium salt and ammonium sulphate or carbonate. It crystallizes in dark yellow prisms with a blue fluorescence, and is very soluble in water and alcohol.

BARIUM PLATINOCYANIDE, $Ba\,Pt(CN)_44H_2O$, may be obtained by boiling the copper salt with barium hydroxide a current of carbon dioxide being afterwards passed

[1] Brochet and Petit.

through the solution to remove the excess of hydroxide, and it may also be prepared by passing hydrocyanic acid into a mixture of platinous chloride and barium carbonate; on evaporating the solution monoclinic crystals of rather large size are obtained, of a sulphur yellow colour, and exhibiting a green fluorescence. When heated to 100° C. the salt becomes anhydrous, the colour changing to white, in which state but little fluorescence is exhibited by the salt.

The **double radium barium platinocyanide** yields red crystals which are self-luminous when freshly prepared, but they lose their luminosity on keeping: this property may, however, be restored by recrystallization.[1]

CALCIUM PLATINOCYANIDE, $CaPt(CN)_4 5H_2O$, prepared like the barium salt, crystallizes in greenish-yellow rhombic crystals, with a violet blue sheen and a green fluorescence.

CADMIUM PLATINOCYANIDE, $CdPt(CN)_4$, is formed as an anhydrous sparingly soluble precipitate when a cadmium salt is precipitated by a soluble platinocyanide. It is yellowish-white in colour, with a blue iridescence: it dissolves in ammonia, from which white needles of the compound, $CdPt(CN)_4(NH_3)_2H_2O$, may be obtained.

CERIUM PLATINOCYANIDE, prepared by double decomposition between cerium sulphate and the barium salt, is obtained in yellow prisms with a blue lustre, and is strongly fluorescent.

COPPER PLATINOCYANIDE, obtained by precipitation, is a green precipitate insoluble in water and acids, but it dissolves in ammonia to form a deep blue liquid, from which blue needles of the compound, $CuPt(CN)_4(NH_3)_2H_2O$, may be obtained.

The cobalt compound is a crystalline flesh-coloured powder, and is obtained by precipitation.

DYSPROSIUM PLATINOCYANIDE, $Dy_2[Pt(CN)_4]_3 \cdot 21H_2O$, prepared from the sulphate and the barium salt, crystallizes in bright red cubic crystals, with a

[1] G. T. Bielby.

green surface sheen, which disappears on dehydration, the crystals becoming first yellow, then white.[1]

The erbium compound yields beautiful red crystals with green metallic reflections which are but feebly fluorescent under ultra violet light.

GADOLINIUM PLATINOCYANIDE, $Gd_2Pt(CN)_4 18H_2O$, is obtained in ruby-red crystals which are green by reflected light.

HYDROPLATINOCYANIC ACID, $H_2Pt(CN)_4$, may be obtained by exactly precipitating the barium salt with sulphuric acid, or by passing hydrogen sulphide through water in which the copper salt is suspended, and may be obtained in crystals by evaporating the solution; the colour of the crystals depends on the amount of water of crystallization. The acid is exceedingly stable, and decomposes carbonates easily: heated to 100° C. it turns first yellow, then white. Heated with strong sulphuric acid, or nitric acid, it is decomposed into hydrocyanic acid and platinous cyanide, and it is soluble in both water and alcohol.

LANTHANUM PLATINOCYANIDE, $LaPt(CN)_4 6H_2O$, occurs in white rhombic prisms of a deep yellow colour, and a blue surface lustre. The crystals effloresce in dry air and lose half their water, the colour changing to scarlet, and they are soluble in water and alcohol.

LEAD PLATINOCYANIDE, obtained by precipitation, is a yellow crystalline powder, soluble in dilute and warm nitric acid, from which it separates on cooling, in small red crystals.

MAGNESIUM PLATINOCYANIDE, $MgPt(CN)_4 7H_2O$, is prepared by exactly precipitating the barium salt with magnesium sulphate. It is obtained in fine prisms, sometimes grouped in rosettes, of a fine red colour by transmitted light, but of a magnificent green colour by reflected light. Heated to 60° C., one molecule of water is given off, the crystals becoming of a yellow colour, at 100° C. the salt becomes white, but still retains two molecules of water, which it holds until heated to 200° C., the white compound changing

[1] *J.C.S.* (1911), ii. 492; *Ber.* (1911), **44**, 1274–84.

to yellow. A double potassium magnesium salt has been obtained, $MgK_2[Pt(CN)_4]_2 14H_2O$,[1] in pale red crystals with a steel-blue lustre.

MERCURIC PLATINOCYANIDE, $HgPt(CN)_4$, is a white precipitate, while the mercurous salt is blue and insoluble. When the latter is boiled the colour changes to white with formation of the mercuric salt.

A **nickelamine platinocyanide** is obtained as a pale violet crystalline powder, by adding a platinocyanide solution to a nickel salt solution to which an excess of ammonia has been added.

POTASSIUM PLATINOCYANIDE, $K_2Pt(CN)_4 3H_2O$, was discovered by Leopold Gmelin, and may be prepared by evaporating a solution of dichloride or dicyanide of platinum in potassium cyanide. It crystallizes in rhombic prisms which are yellow by transmitted light and blue by reflected light; the crystals effloresce in dry air and turn light red, and on further heating the crystals become white. The potassium compound forms a number of double salts with other soluble platinocyanides, which are generally of a brighter and deeper colour than the components. The double sodium potassium salt, $NaKPt(CN)_4 6H_2O$, crystallizes in monoclinic crystals, deep orange by transmitted light and deep purple to blue by reflected light, with a green fluorescence. The potassium strontium salt, $K_2Sr[Pt(CN)_4]_2$, forms monoclinic prisms of a yellow colour with a blue iridescence. The potassium lithium salt forms rhombic crystals of an orange-red colour, with a blue sheen, and a yellow fluorescence. The double potassium barium and potassium calcium salts have also been prepared.

RUBIDIUM PLATINOCYANIDE, $Rb_2Pt(CN)_4 3H_2O$, forms pale green crystals, crystallizing in the monoclinic system without iridescence, but with a sky-blue fluorescence. A rubidium lithium salt, $RbLiPt(CN)_4$, in rhombic yellow crystals with a blue iridescence and green fluorescence, has been described.

[1] Hadow.

SILVER PLATINOCYANIDE, obtained by precipitation, is a white curdy insoluble compound. If precipitated in the presence of an excess of ammonia, the compound, $Ag_2Pt(CN)_4(NH_3)_2$, is obtained in colourless needles, soluble in hot ammonia liquor, but insoluble in water.

SODIUM PLATINOCYANIDE, $Na_2Pt(CN)_4 3H_2O$, is prepared in a similar manner to the potassium salt, and crystallizes in long lustrous, colourless needles which are stable in the air but become anhydrous at 120° to 125° C. They do not fluoresce, nor are they attacked by chlorine like the potassium salt.[1]

STRONTIUM PLATINOCYANIDE, $SrPt(CN)_4 5H_2O$, crystallizes in colourless monoclinic crystals, free from iridescence, but exhibiting a strong violet fluorescence; during dehydration by heat the salt passes through many colour changes and finally at 150° C. becomes white and anhydrous. The anhydrous salt and the coloured hydrates are only faintly fluorescent.

SCANDIUM PLATINOCYANIDE, $Sc_2[Pt(CN)_4]_3 21H_2O$, prepared from the barium salt and scandium sulphate, is a very soluble salt and crystallizes in monoclinic prisms which are insoluble in alcohol. It is crimson by transmitted light and metallic green by reflected light.[2] The hydrate, $Sc_2[Pt(CN)_4]_3 18H_2O$, is obtained in yellow crystals.[3]

The **URANYLPLATINOCYANIDE,** $UrO_2Pt(CN)_4$, does not fluoresce when exposed to ultraviolet light or to radium emanations.

YTTRIUM PLATINOCYANIDE, $Y_2[Pt(CN)_4]_3 21H_2O$, forms red crystals with a metallic green reflection which exhibits a feeble red fluorescence.

The addition of a platinocyanide solution to an ammoniacal solution of a zinc salt yields colourless crystals of the compound $ZnPt(CN)_4(NH_3)_2$.

Attempts to produce compounds of platinic cyanide by oxidation of the platinocyanides, by the action of

[1] S. Wilm, *Z. anorg. Chem.*, **4**, 298–99.
[2] W. Crookes, *Chem. News*, **101**, 49.
[3] A Orlov, *Chem. Zeit.* (1912), **36**, 1407–8.

chlorine or nitric acid, were made by Weselsky [1] and by Knap,[2] and they obtained products which crystallized in the form of crystals with a strong coppery lustre. The general formula, $M_2Pt(CN)_5$, was given to these salts, which were considered to be platinicyanides. The method employed to obtain them was exactly similar to the general method for the preparation of ferricyanides from ferrocyanides, by passing chlorine into the solution of the platinocyanides.

Hadow [3] reinvestigated these salts, and proved that they could not be platinicyanides as the ratio between base, platinum, and cyanogen in the oxidation products was the same as in the platinocyanides, but that the former contained a certain proportion of chlorine when that element had been used as an oxidizing agent, and also that when the oxidation compound was reduced to the platinocyanide, no cyanide appeared to be formed.

From these facts Hadow considered these salts as double salts of unchanged platinocyanide and perchloroplatinocyanide, thus :

$$(K_2Pt(CN)_4)_6Cl_2 = 5K_2Pt(CN)_4 + K_2Pt(CN)_4Cl_2,$$

and this explanation was confirmed by the formation of the copper coloured potassium compound by crystallizing together potassium platinocyanide and potassium perchloroplatinocyanide.

Levy, however, who has again investigated these salts,[4] has shown that the formula of Hadow was incorrect, and that the true composition of the potassium double salt is :

$$6K_2Pt(CN)_4K_2Pt(CN)_4Br_216H_2O,$$

and that the ratio of platinocyanide to perchloro or perbromoplatinocyanide is as 6 : 1 and not as 5 : 1 as stated by Hadow.

The salt above mentioned is obtained in long needles with a strong coppery lustre, readily soluble in water

[1] *J. pr. Chem.* (1856), **69**, 276. [2] *Ann.* (1872), **42**, 111.
[3] *Quart. J., Chem. Soc.* **13**, 106. [4] *T.C.S.* (1912), 1082.

to form a yellow solution, and at 120° C. the salt becomes anhydrous, and changes to a dark bluish green.

The amount of bromocompound can be determined by estimating the amount of iodine liberated from potassium iodide solution, or by estimating the amount precipitated by the addition of zinc sulphate, zinc platinocyanide being insoluble in water while the perbromo compound of zinc is soluble.

It would also appear from Levy's investigations that no double salt exists in any other ratio than that of as 6 : 1, and also that no compound corresponding to a platinicyanide of the formula $M_2Pt(CN)_5$ exists.

The formation of a compound containing the group SO_4 was first noted by Hadow,[1] but Levy,[2] by the action of lead peroxide or manganese dioxide on potassium platinocyanide in presence of sulphuric acid, obtained a product in bronze-coloured needle crystals, to which he assigned the probable formula $9K_2Pt(CN)_4K_2Pt(CN)_4SO_4$. By substituting hydrogen peroxide for the lead peroxide, a different compound was obtained free from the SO_4 group, to which he gave the formula :

$$K_7Pt_4(CN)_{16}6H_2O = 3K_2Pt(CN)_4KPt(CN)_46H_2O.$$

This compound crystallizes in fine bronze crystals readily soluble in water, forming a colourless solution. At 120° C. it becomes anhydrous, and is reconverted into potassium platinocyanide by the addition of potassium cyanide. Carbon dioxide may be substituted for the sulphuric acid with equal success.

The oxidation of lithium platinocyanide by hydrogen peroxide and sulphuric acid results in the formation of a compound which is similar but not identical to the potassium salt, in the form of fine copper-coloured crystals having the composition $2Li_2Pt(CN)_4LiPt(CN)_4$.

Sodium Platinocyanide oxidized in a similar manner yielded copper-red crystals of the salt, $2Na_2Pt(CN)_4NaPt(CN)_4$.

[1] *Quart. J. Chem. Soc.* (1861), **14**, 106. [2] *L.c.*

By the oxidation of hydroplatinocyanic acid in acid solutions, and the solution carefully evaporated, a white substance was first obtained, which became pink, brown and olive-green. These different coloured substances are one and the same compound, with different proportions of combined water; and it is considered by Levy to be hydroplatinicyanic acid. The solution of the compound in water liberates iodine from potassium iodide, and produces no precipitate in moderately dilute solutions with salts of zinc or copper. With silver nitrate a light brown flocculent precipitate of silver platinicyanide, $AgPt(CN)_4$, is obtained, and when boiled with sulphurous acid, platinocyanide is generated. The solution, treated with potassium platinocyanide, yields bronze needles similar to the product formed by the action of hydrogen peroxide and sulphuric acid on potassium platinocyanide.

The green product has a composition agreeing with the formula $HPt(CN)_4 2H_2O$, and is formed from the platinocyanide and hydrogen peroxide thus :

$$H_2O_2 + 2H_2Pt(CN)_4 = 2H_2O + 2HPt(CN)_4,$$

and reacts with potassium iodide thus :

$$KI + HPt(CN)_4 = KHPt(CN)_4 + I.$$

Platinicyanides of other bases have also been described by Levy, but as the action of ordinary twenty volumes hydrogen peroxide only partially oxidized the platinocyanides of the stronger bases he substituted " perhydrol," a more concentrated solution, and by the action of this reagent in the presence of a little dilute sulphuric acid he succeeded in obtaining the following platinicyanides :

Lithium Platinicyanide, $LiPt(CN)_4 2H_2O$, a colourless salt which on dehydration became first yellow then brownish-red.

Potassium Platinicyanide, $KPt(CN)_4$, as a dark blue product, on evaporation of the aqueous solution on the water-bath, which turned white when moistened with water.

Rubidium platinicyanide, $RbPt(CN)_4$, is a white compound which turns pink in dehydration.

Sodium platinicyanide, $NaPt(CN)_4$, obtained in purple needle crystals, which turn white on the addition of water.

These platinicyanides are rapidly decomposed in neutral solutions and do not exist in alkaline solutions.

POTASSIUM CYANIDE, KCN, may be prepared by passing dry hydrocyanic acid into alcoholic potassium hydroxide solution, as a white crystalline precipitate which may be filtered on the vacuum pump, washed with alcohol, and dried over sulphuric acid. It crystallizes from water in anhydrous crystals which are colourless and generally smell of hydrocyanic acid due to the combined action of moisture and carbon dioxide from the atmosphere. It is very fusible, melts at about 622° C., and solidifies on cooling to a white crystalline mass. When heated to a white heat it volatilizes unchanged, if air and moisture are absent, and at a red heat it reduces carbon dioxide to monoxide with formation of a cyanate.[1]

The salt has an alkaline reaction, is very poisonous, deliquesces in moist air, and dissolves readily in water, but is insoluble in alcohol. Aqueous solutions keep fairly well out of air contact, but after a considerable time a small portion is converted into ammonia and potassium formate. This decomposition takes place somewhat more readily on boiling. The salt is rapidly oxidized to cyanate when fused in contact with the air, or with easily reducible oxides such as lead oxide or manganese dioxide.

Potassium cyanide was used to a considerable extent in the extraction of gold from its ores by the cyanide process, but has been generally supplanted by the cheaper sodium cyanide. The potassium cyanide of commerce usually consists of a mixture of sodium and potassium cyanide.

RHODIUM·CYANIDE, $Rh(CN)_3$, is precipitated by the addition of acetic acid to a solution of the double

[1] Eiloart, *Chem. News* (1886), **54**, 88.

potassium rhodicyanide as a red insoluble compound. The double salt may be prepared by the method described by E. Leidié.[1] Hydrocyanic acid is added to a solution of the freshly prepared rhodic hydroxide in strong caustic potash, the solution is filtered and slowly evaporated in vacuo over sulphuric acid. After two recrystallizations the double cyanide, $K_3Rh(CN)_6$, is obtained in faintly yellow monoclinic prism. The crystals are anhydrous, very soluble in water, and are decomposed by alkalis or strong hydrochloric acid, and give precipitates with salts of iron or copper similar to other complex cyanides.

The potassium salt may also be formed by fusing potassium cyanide with rhodium ammonium chloride.[2]

RUTHENIUM CYANIDE. When potassium cyanide is fused with the double ruthenium ammonium chloride, small white crystals of double ruthenocyanide of potassium, $K_4Ru(CN)_6 3H_2O$, isomorphous with potassium ferrocyanate,[2] are obtained.

The acid may be prepared in a manner similar to the preparation of hydroferrocyanic acid by the addition of hydrochloric acid and ether, in lustrous crystals, $H_4Ru(CN)_6$, which are easily soluble in water and alcohol: but when heated in aqueous solution decompose with evolution of hydrocyanic acid.

The solution of the double salt yields coloured precipitates with many of the metallic salts, but no simple cyanide of ruthenium has yet been isolated.

SILVER CYANIDE, AgCN, is a white curdy precipitate formed when an alkaline cyanide solution is added to an excess of silver nitrate solution. The precipitate very closely resembles silver chloride in appearance, but differs from that body in being soluble in hot nitric acid. It is soluble in aqueous ammonia, from which it crystallizes combined with ammonia, $AgCNNH_3$, in monoclinic crystals (silver chloride crystallizes from ammonia in octahedra); the compound loses ammonia and its crystalline form on

[1] *Compt. rend.*, 130 [2], 87–90. [2] Claus, *J.* (1855), 444.

exposure to the air or on washing. The hydrazine compound, $AgCNH_2N_4$, has also been obtained.[1]

Silver cyanide does not darken on exposure to light, but when heated to 320° to 350° C. it melts and decomposes to metallic silver and cyanogen. Part, however, of the cyanogen is converted to paracyanogen, which may be driven off by further raising the temperature. It is practically unattacked by nitric acid in the cold, but completely decomposed by hydrochloric acid into silver chloride and hydrocyanic acid. It is also decomposed by hydrogen sulphide and alkaline sulphides into silver sulphide and hydrocyanic acid and an alkaline cyanide respectively.

An aqueous solution of calcium hypochlorite decomposes silver cyanide with violent effervescence evolving carbon dioxide, nitrogen and some cyanogen.

Silver cyanide dissolves easily in a solution of the alkaline cyanides, forming double salts of the type $M'Ag(CN)_2$.

These double salts are easily decomposed by acids with precipitation of silver cyanide; if hydrochloric acid or a chloride is also present the silver cyanide is also decomposed. The salts crystallize well and are stable, and are completely decomposed with precipitation of silver sulphide by alkaline sulphides and by sulphuretted hydrogen. In the latter case, however, the silver is not completely removed from solution if an excess of alkaline cyanides are present.

The potassium salt, $KAg(CN)_2$, crystallises in regular octahedra, and the following salts have been described, $NaAg(CN)_2$; $3AgCN.2KCN.NaCN$,[2] $AgCNTlCN$.[3] The soluble salts give precipitates with manganese, zinc, cadmium, and lead salts, etc., which are probably mixed cyanides. Mercuric chloride solution added to a soluble double silver cyanide converts the whole of the cyanogen into mercuric cyanide.

[1] Franzer and Lucking, *Z. anorg. Chem.* (1911), **70**, 145–56.
[2] Bauf, *Ann. Chim. Phys.* (3), **53**, 462.
[3] Fronmüller, *Ber.*, **11**, 91.

SODIUM CYANIDE, NaCN, may be prepared by any of the general methods for making the potassium salt, to which it is similar in its reactions. It may be obtained in a state of practical purity by fusing dry sodium ferrocyanide with metallic sodium; the fused product when cooled forms a hard white crystalline mass which melts at 561.7° C.

A strong aqueous solution of sodium cyanide deposits crystalline plates containing two molecules of water of crystallization, which melt when heated to 34° C.: crystals deposited from solution above this temperature are anhydrous. According to Joannis [1] two hydrates may be obtained from hydrated alcohol by crystallizing the salt at different temperatures, $NaCN2H_2O$ and $2NaCNH_2O$.

Sodium cyanide in the solid state may be kept unaltered out of air contact, but the strong solution, if exposed to the air, gradually turns brown. If, however, the solution is kept out of air contact for a considerable time, no coloration takes place, but some decomposition occurs with formation of ammonia, thus:

$$NaCN + 2H_2O = NaHCO_2 + NH_3.$$

Sodium cyanide is now manufactured on a large scale for use in the extraction of gold from its ores in place of potassium cyanide, which it has almost driven out of the market.

STRONTIUM CYANIDE, $Sr(CN)_24H_2O$, is very similar to the barium salt and is prepared in the same manner. It is very unstable, giving off considerable quantities of hydrocyanic acid when boiled under atmospheric pressure, but may be obtained in orthorhombic crystals if evaporated with care under a vacuum. The crystals are said to be very deliquescent.[2]

THALLIUM CYANIDE, Tl(CN), may be obtained from the barium cyanide by precipitation with thallious sulphate. It is soluble in water and alcohol, and in

[1] *Ann. Chim. Phys.* (15). **27**, 482.

[2] Joannis, *Ann. Çhim. Phys.*, **5**, 27, 482.

excess of alkaline cyanides. A solution of thallious cyanide dissolves silver cyanide and forms a double salt which may be obtained in crystals. The double zinc and mercury cyanides are also known, $2TlCNZn(CN)_2$; $2TlCNHg(CN)_2$.

TITANIUM CYANIDE. No true cyanide of titanium is known. A compound which occurs in copper-coloured crystals as a furnace product from blast furnaces, has a composition of a cyanonitride, Ti_5CN_4, which may be a double compound of a cyanide and a nitride, $Ti(CN)_23Ti_3N_2$. By fusion with potash it is decomposed into potassium titanate and ammonia. It may also be prepared by igniting potassium ferrocyanide and titanium oxide,[1] or by heating potassium cyanide in the vapour of titanium chloride.

The compound is volatile at a high temperature, and is not attacked by aqueous sulphuric, or nitric acid. According to B.P., 1841, 1908,[2] the titanium cyanonitride when fused with dry sodium carbonate and carbon forms sodium cyanide, with barium oxide and chloride a mixture of cyanide, and cyanamide; and with calcium oxide and chloride, cyanamide only is formed.

URANIUM CYANIDE. No cyanide of uranium has yet been isolated. When a uranium salt solution is precipitated by the addition of potassium cyanide, the precipitate consists of the hydroxide only.[3] Wittstein, however, states [4] that a yellow precipitate is obtained which is soluble in excess.

VANADIUM CYANIDE is said to be obtained as a dark brown gelatinous precipitate soluble in excess, by direct precipitation, but when this solution is evaporated, hydrocyanic acid is evolved.

YTTRIUM CYANIDE is prepared by dissolving the hydroxide in hydrocyanic acid: by evaporation, the compound may be obtained in efflorescent crystals.

ZINC CYANIDE, $Zn(CN)_2$, is obtained by direct

[1] Wöhler, *A.*, **73**, 34; **74**, 212.
[2] Badische Anilin und Soda Fabrik.
[3] Rammelsburg, *P.*, **39**, 2. [4] *R.P.*, **63**, 214.

precipitation as a white anhydrous amorphous precipitate, which is quite stable in the air, and may be heated out of air contact to about 1000° C. before decomposition takes place.[1] The cyanide dissolves readily in the solutions of the alkaline cyanides to form double salts. The barium salt, $BaZn(CN)_4 2H_2O$, is very soluble in water and crystallizes well. The calcium salt is exceedingly soluble and impossible to obtain in crystals from an aqueous solution, but unlike the solution of calcium cyanide it may be evaporated with but little decomposition. The potassium salt, $K_2Zn(CN)_4$, may be obtained in anhydrous colourless octahedral crystals. The sodium salt, which is very soluble, crystallizes after some time, containing three, but not six molecules of water as usually stated, $Na_2Zn(CN)_4 3H_2O$, which become anhydrous at 100° C. The strontium salt is also very soluble.

The soluble double salts yield precipitates with the salts of lead, nickel, cobalt, etc.

The soluble double zinc cyanides are decomposed in solution by the addition of caustic alkalis, an alkaline cyanide and a soluble zincate being formed,[2] and the total cyanide in such a solution can be accurately titrated with standard silver nitrate solution, if potassium iodide is used as an indicator.

The addition of a mineral acid to a solution of a double cyanide first precipitates zinc cyanide, but a further addition of hydrochloric or sulphuric acid completely decomposes it into hydrocyanic acid and a zinc salt.

Vanel[3] has prepared the mercury double salts, $Zn(CN)_2Hg(CN)_2HgCl_2 6NH_3$ and $Zn(CN)_2Hg(CN)_2HgCl_2 6H_2O$. The hydrazine compound, $Zn(CN)_2(N_2H_4)_2$, has also been prepared.

[1] Truttie. [2] W. R. Feldmann, *J.S.C.I.* (1894), 952.
[3] *Compt. rend.*, 106, 1080.

CHAPTER IV

IRON CYANOGEN COMPOUNDS

THE FERROCYANIDES

GENERAL REACTIONS AND PROPERTIES. The addition of a ferrous salt or of ferrous hydroxide to a solution of an alkaline cyanide results in the formation of a type of cyanogen compound differing greatly in its general properties and reactions from the simple cyanides. The ferrous iron unites with the cyanogen to form the tetrad negative radicle ferrocyanogen, $''''Fe(CN)_6$, and a very large number of salts of this radicle of the types $M'_4Fe(CN)_6$ and $M''_2Fe(CN)_6$ are known.

The iron in the complex ferrocyanogen radicle cannot be detected by the usual reagents; neither alkaline hydroxide nor sulphides yield any of the characteristic reactions for iron. The complex ion, $''''Fe(CN)_6$, does, however, further ionize to a limited extent, thus, $''''Fe(CN)_6 = Fe + 6CN$. This action, which is but slight in the solutions of the alkali metals, is somewhat more marked in the solutions of the alkaline earth metal ferrocyanides, and of lithium, magnesium, and ammonium ferrocyanides, from the boiling solution of which traces of hydrocyanic acid are evolved.

Clennel [1] has shown that a high reading is obtained in the titration of a cyanide with nitrate of silver solution, in the presence of a soluble ferrocyanide, which must be due to some cyanogen ions of the ferrocyanide.

[1] *Chem. News* (1895), **72**, 227.

When a few drops of a silver nitrate solution are added to a dilute solution of potassium ferrocyanide, the precipitate at first formed redissolves on agitation, and as much as 2 c.c. of N/10 silver nitrate solution can be added to 100 c.c. of a one per cent. solution of potassium ferrocyanide before a permanent opalescence occurs. On warming the solution an increased amount of silver nitrate is required.

The addition of an alkaline hydroxide, carbonate or alkali metal salt prevents the dissociation of the ferrocyanogen ion, and a permanent precipitate of silver ferrocyanide is obtained on adding one drop of the silver solution to the ferrocyanide solution containing these salts.

This dissociation of the ferrocyanogen complex to form cyanogen ions is the probable explanation of the complete conversion of the cyanogen of the ferrocyanide to mercuric cyanide, when a ferrocyanide is boiled with mercuric chloride; mercury cyanide being practically undissociated in solution.

With the exception of barium, the ferrocyanides of the alkali and alkaline earth metals, including lithium and magnesium, are easily soluble in water, but insoluble in alcohol, the barium salt being but sparingly soluble in water. All the soluble salts crystallize from their aqueous solutions in more or less yellow crystals containing varying amounts of water of crystallization. The lithium salt is exceedingly soluble in water and the crystals are deliquescent, and in this latter property differs from the other soluble ferrocyanides.

The salts of the heavy metals are insoluble in water and are chiefly characterized by the wide range of colour of the different metallic compounds, a property of great value in analytical chemistry.

With the exception of the silver salt, the composition of the precipitates obtained by adding a soluble ferrocyanide to a metallic salt varies with the conditions of the precipitation, and with the particular ferrocyanide used. Pure insoluble metallic ferrocyanides can only be obtained by precipitating hydroferro-

cyanic acid with a metallic salt in excess, or by the addition of a solution of calcium ferrocyanide to an excess of the chloride or nitrate of the metal.[1]

The insoluble metallic ferrocyanides with the exception of the pure manganese compound are amorphous, and when air-dried generally contain a considerable quantity of water in combination; part of this combined water may be removed by exposing the substance for some time to a dry atmosphere, by placing it over calcium chloride or concentrated sulphuric acid; and a greater amount if kept for some weeks over phosphoric pentoxide. When heated to 100° C. a further quantity of water is driven off. But with few exceptions it has been found impossible to remove all the combined water, either by prolonged drying over powerful dehydrating agents, or by heating, for although more and more water is driven off the dry compound as the temperature rises, decomposition of the ferrocyanide occurs in the majority of cases before all the water is driven off. Many of the ferrocyanides of the heavy metals, if exposed to the air after thorough drying and heating to 100° C., reabsorb all that lost at 100° C., and frequently an amount equal to that contained in the original air-dried sample.

Considerable doubt exists as to whether this water can be considered as chemically combined or not, though several facts tend to point to some form of combination. Thus in the simpler insoluble compounds, the amount of water retained by the air-dried material generally agrees with a definite whole number of molecules of water to one molecule of the ferrocyanide compound; and again in a few cases a colour change takes place on drying: for example, cupric calcium ferrocyanide, when air dried, is a light brown powder and contains water equivalent to twelve molecules: on heating to 100° C. a loss of exactly two-thirds of its total water takes place, accompanied by a marked change of colour, the light brown changing to a magnificent violet. When again exposed

[1] H. E. W., *Chem. World*, vol. i. p. 43.

to the air, the whole of the water lost at 100° C. is exactly reabsorbed, and the colour passes back to the original light brown. Several other compounds, on heating to 100° C., alter in colour with loss of water.

This remarkable colour change due to the loss of water tends to support the view that the water held by these compounds is combined and not merely held by the colloidal nature of the compound.

A large series of double salts of the ferrocyanide are known and can be classed under two heads: (1) The sparingly soluble double salts, which are formed by the interaction of the alkali metal ferrocyanides with the ferrocyanides of the alkaline earth metals; potassium and ammonium ferrocyanides forming double salts with calcium, barium, strontium and magnesium ferrocyanide, and sodium ferrocyanide with the calcic and magnesium compound.

(2) The insoluble double salts: these compounds are prepared by the interaction of the soluble ferrocyanides with the insoluble heavy metal ferrocyanides, and can generally be prepared by adding the heavy metal salt solution such as the chloride, or nitrate, to a large excess of the soluble ferrocyanide; preferably in the presence of an excess of the chloride of the metal of the ferrocyanide used. By this method compounds such as $CuK_2Fe(CN)_6$; $CuCaFe(CN)_6$, and $CoK_2Fe(CN)_6$ are prepared. By varying the method of precipitation, compounds of the type $M''_3K_2[Fe(CN)_6]_2$; $M''_4K_4[Fe(CN)_6]_3$, and $M''_6K_8[Fe(CN)_6]_5$ can be prepared, where M'' represents an atom of a divalent metal when potassium ferrocyanide is used.

The alkali metal ferrocyanides possess a much greater tendency to combine with the heavy metal ferrocyanides than the alkaline earth salts. In the latter case, if the metallic salt is in large excess, the precipitate is found almost entirely free from the base of the ferrocyanide, whereas with the former it is quite impossible to produce an insoluble metallic ferrocyanide free from the alkali metal, however large the excess of metallic salt used. This alkali metal

retained by the ferrocyanide cannot be removed by washing with water, either before, or after, drying and grinding.

When the percentage is small it is usually considered to be not in combination, but to be tenaciously held by the colloidal nature of the precipitate. This view, however, is probably in error, for a careful examination of these compounds prepared under definite conditions reveals the fact that the alkali metal exists in a definite and fairly simple ratio to the ferrocyanide, and that the amount is a constant for ferrocyanides prepared under the same condition. As these metallic precipitates are mostly colloidal the molecule is probably somewhat complex, and may consist of a definite number of molecules of the pure metallic ferrocyanide with one or more molecules of the double salt; thus taking the cupric ferrocyanides for example we have $Cu_2Fe(CN)_6$ and $CuK_2Fe(CN)_6$ as representing the two extremes of the potassium-cupric series and the known compounds $Cu_3K_2[Fe(CN)_6]_2 = Cu_2Fe(CN)_6 + CuK_2Fe(CN)_6$; $Cu_4K_4[Fe(CN)_6]_3 = Cu_2Fe(CN)_6 + 2CuK_2Fe(CN)_6$, and $Cu_6K_8[Fe(CN)]_5 = Cu_2Fe(CN)_6 + 4CuK_2Fe(CN)_6$, as intermediate compounds.

Some of the insoluble ferrocyanides, particularly those containing a large proportion of alkali metal in combination, when moistened with water after drying in air, swell up to a pasty mass like gelatine.

With the exception of the copper salt, all the soluble and insoluble ferrocyanides are decomposed by repeatedly boiling with strong hydrochloric acid into hydroferrocyanic acid and a metallic chloride; the copper compound, however, is converted into the acid salt, $CuH_2Fe(CN)_6 4H_2O$. By using a more dilute acid, the cobalt, nickel, and manganese hydrogen salt can be prepared.

The action of nitric acid on the soluble and sparingly soluble ferrocyanides is very complex, some of the ferrocyanides being entirely decomposed and the remainder converted first into ferricyanides and finally into nitroferrocyanides.

The ferrocyanides of the heavy metals are generally converted into ferricyanides by boiling with nitric acid. The cupric and ferric salts, however, when boiled in the dry powdered state with strong nitric acid, are converted into compounds of the formula $Cu_5(Fe'''_2Fe''(CN)_{18})$ and $Fe''_{3.7}[Fe''Fe'''(CN)_{12}]_3 = Fe'''_4[Fe''(CN)_6]_3 + 3Fe'''Fe'''(CN)_6$, only 50 per cent. of the total ferrocyanides being oxidized to ferricyanides, and the blue colour of the iron salt changing to a fine green.

When boiled with dilute sulphuric acid, the ferrocyanides of the alkali metals, including magnesium, are decomposed, 50 per cent. of the total cyanogen is evolved as hydrocyanic acid and the remainder precipitated as a white precipitate of a double ferrous ferrocyanide of the alkali metal used, thus :

$$2K_4Fe(CN)_6 + 3H_2SO_4 = Fe''K_2Fe(CN)_6 + 6HCN + 3K_2SO_4.$$

The ferrocyanides of the alkaline earth metals, including lithium and lead, behave somewhat differently under the above treatment, two-thirds of the total cyanogen being evolved in the form of hydrocyanic acid, and the remaining one-third is left as the insoluble pure ferrous ferrocyanide :

$$3Ca_2Fe(CN)_6 + 6H_2SO_4 = Fe''_2Fe(CN)_6 + 12HCN + 6CaSO_4.$$

This reaction with dilute sulphuric acid also takes place with other dilute mineral acid, and with oxalic and acetic acids, and is the general method for preparing hydrocyanic acid from soluble ferrocyanides.

When any dry ferrocyanide, either soluble or insoluble, is treated with concentrated sulphuric acid, a white pasty mass results, and on heating complete decomposition of the ferrocyanide subsequently takes place with effervescence, carbon monoxide, carbon dioxide, and sulphurous acid gases are evolved, and ferric and ammonium sulphate, together with the sulphate of the base of the ferrocyanide, are formed. It has been stated that nitrogen and nitrogen compounds are sometimes evolved with the gases during

this decomposition. This, however, is not the case if sufficient excess of sulphuric acid is present, and the ferrocyanide dried before treatment; the whole of the nitrogen of the cyanogen is then converted into ammonium sulphate quantitatively, thus:

$$2K_4Fe(CN)_6 + 24H_2SO_4 = 4K_2SO_4 + Fe_2(SO_4)_3 + 6(NH_4)_2SO_4 + 11SO_2 + 10CO_2 + 2CO.$$

This reaction, however, is not quite so simple as shown here, for if the reaction is stopped before the effervescence is finished some carbonylferrocyanides can be shown to exist in the acid mixture by the violet colour formed on dilution.

Chlorine gas passed through a solution of a ferrocyanide abstracts one equivalent of the base of the ferrocyanide, and oxidizes the ferrous iron of the ferrocyanogen radicle to ferric iron forming ferricyanides:

$$2K_4Fe''(CN)_6 + Cl_2 = 2KCl + 2K_3Fe'''(CN)_6.$$

If the gas is passed through suspensions of the freshly precipitated metallic ferrocyanides, these are also generally oxidized completely to the corresponding ferricyanides; the ferrocyanides of zinc, copper, lead, cadmium, etc., can be oxidized in this manner. The action of the gas on suspension of prussian blue is, however, somewhat different, the oxidation being incomplete, only three-quarters of the total ferrocyanides being converted into ferricyanides; the product thus formed is of a fine deep green colour and consists of a compound of ferric ferro- and ferricyanide.

Soluble ferrocyanides can also be converted into ferricyanide by bromine, or other oxidizing agents, such as potassium permanganate, chromic acid, etc.

The addition of iodine to a solution of a ferrocyanide forms first a ferricyanide, and then by further action a solution of the so-called "perferricyanide" is obtained, an unstable compound which will be more fully discussed later.

By boiling any ferrocyanide, whether soluble or

insoluble, with recently precipitated mercuric oxide, decomposition occurs, the ferrocyanogen group is broken up, iron and the metallic base of the ferrocyanide are thrown out of combination as hydroxides, and mercuric cyanide remains in solution :

$$2K_4Fe(CN)_6 + 7HgO + 4H_2O = 6Hg(CN)_2 + Fe_2O_3 + 8KOH + Hg.$$

A similar reaction takes place when the ferrocyanide is boiled with mercuric chloride.

When a solution of a ferrocyanide is boiled with cuprous oxide in contact with air, ferric hydroxide and sometimes black ferrosoferric hydroxide is slowly precipitated, and a cuprocyanide remains in solution ; the addition of a caustic alkali hastens the action, the cuprous oxide destroying the ferrocyanogen complex much in the same way as mercuric oxide, but its action is much slower. Cuprous chloride or thiocyanate also decompose ferrocyanides, but their action is incomplete ; part of the ferrocyanide is decomposed to form double cuprocyanides and part is precipitated as a ferrosocuproferrocyanide.

When boiled with the cuprous chloride in acid solution complete decomposition of the ferrocyanide takes place, the whole of the cyanogen is driven off as hydrocyanic acid ; for this reaction only a small proportion of cuprous chloride is necessary ; about 3 per cent. of the total ferrocyanide present—the best results are obtained when the cuprous chloride is dissolved in a few drops of hydrochloric acid before adding it to the ferrocyanides.

A solution of ammoniacal silver nitrate also completely decomposes a ferrocyanide when heated, with formation of an ammonium silver cyanide.

If the dry powdered ferrocyanide is intimately mixed with an excess of dry ammonium chloride and gently heated, all the cyanogen is evolved as ammonium cyanide :

$$K_4Fe(CN)_6 + 6NH_4Cl = 6NH_4CN + 4KCl + FeCl_2,$$

or $$Fe_4[Fe(CN)_6]_3 + 18NH_4Cl = 18NH_4CN + 4FeCl_3 + 3FeCl_2$$

With the exception of the ammonium salt, most of the soluble ferrocyanides are very stable, and their solutions can be evaporated with but slight loss. The magnesium and lithium salt decomposes slightly more than the salts of sodium or potassium, when the solutions of these salts are boiled, but the ammonium salt is very unstable; on boiling its solution ammonium cyanide is evolved, and a green ferrosoferric ferrocyanide precipitated.

The water of crystallization of the soluble ferrocyanides and their double salts is with few exceptions completely driven off at 100° C.

According to S. H. C. Briggs,[1] the soluble ferrocyanides exist in two isomeric modifications designated by him as "α" and "β" ferrocyanides. The "α" salts are described as of a light lemon colour and the "β" salts amber-coloured, no difference in composition has been detected, and the general reactions are identical in both cases.

The "α" modification is the most common form and the "β" may be prepared from the "α" form by acidifying a saturated solution with 1 per cent. of acetic, or other acid and keeping the solution out of air contact for twenty-four hours; the addition of alcohol then precipitates the "β" salt as a cream-coloured powder.

Heating the "β" compound with alkalis or cyanides reconverts it into the pale yellow "α" salt. The explanation of these two modifications put forward by Briggs is that they are stereoisomerides, and that from theoretical considerations of the formula of, say, potassium ferrocyanide, two such stereoisomerides are possible.

Most of the ferrocyanides practically resist the action of boiling solutions of an alkaline polysulphide, but little thiocyanate being formed. If, however, the ferrocyanide is fused with an alkali and sulphur, or the aqueous solution heated under pressure with an aqueous solution of a polysulphide to a temperature

[1] *T.C.S.*, **99**, 1019–35.

corresponding to about 30 lb. per square inch, complete conversion of the ferrocyanide to thiocyanate occurs and the iron precipitated as a green double sulphide of ferrous iron and the alkali metal employed.

By heating under pressure to 150 lb. per square inch with an aqueous solution of a thiosulphate, ferrocyanides are also converted quantitatively into thiocyanates :

$$K_4Fe(CN)_6 + 6K_2S_2O_3 = 6KCNS + FeS + 2K_2SO_3 + 3K_2SO_4.$$

Carbon dioxide passed through a solution of potassium ferrocyanide heated to 70° to 80° C. liberates some hydrocyanic acid, with formation of a small precipitate of ferrous potassic ferrocyanide.[1]

Several of the insoluble ferrocyanides are decomposed when boiled with a solution of disodium hydrogen phosphate, sodium ferrocyanide being formed in solution, and an insoluble phosphate precipitated. With cupric ferrocyanide the action only takes place on boiling, a blue precipitate of cupric phosphate being formed : on cooling a reverse action takes place, the copper phosphate being converted into the red-brown cupric sodium ferrocyanide.

When the dry alkali metal ferrocyanides are heated with an excess of an oxidizing agent, such as manganese dioxide, two-thirds of the total cyanogen is left in the form of a cyanate of the alkali metal.

Sparingly soluble salts are formed from the soluble ferrocyanides by the organic ammonias and the alkaloids generally, such as dimethylaniline, strychnine, etc., which sometimes affords a convenient method for separating these bodies from other compounds.

Many of these sparingly soluble precipitates are only formed in acid solution, and are double hydrogen salts of the type $M_2H_2Fe(CN)_6$, *e.g.* dimethylaniline hydrogen ferrocyanide, $[C_6H_5N(CH_3)_2H]_2H_2Fe(CN)_64H_2O$.

The very striking and characteristic colours produced when the salt of iron, and copper are added to

[1] W. Autenreilt, *Arch. Pharm.*, **231**, 99–109.

a soluble ferrocyanide, serve as a means of detecting either the ferrocyanide, or the metallic salt. Ferric salts produce a deep blue bulky precipitate which affords an exceedingly delicate test. Ferrous salts produce at first a white precipitate with generally a faint blue tinge, which rapidly oxidizes to blue in the air, and copper salts form a very gelatinous chocolate-coloured precipitate.

The ferrocyanides of the alkali metals are used to a limited extent in the arts in the manufacture of the pigment prussian blue, in the dyeing and weighing of silk and other fibre, in calico printing, as a chemical reagent, and for the case-hardening of steel, but the principal use to which the great bulk of the ferrocyanide now manufactured is put is as a raw material for the production of cyanides.

The ferrocyanides exist in small quantities in spent oxide of iron, a waste product obtained in the purification of coal gas, and also in cyanogen mud, a black evil-smelling sludge obtained by scrubbing the hydrocyanic acid from crude coal gas with a solution of ferrous sulphate; and occur as the sodium salt to a limited extent in the mother liquor of alkali made by the Leblanc soda process.

THE METALLIC FERROCYANIDES

ALUMINIUM FERROCYANIDE, $Al_4[Fe(CN)_6]_3XH_2O$, is prepared in the pure state only by precipitation of the hydrogen or calcium salt with an excess of aluminium chloride. It is obtained as a highly gelatinous precipitate, which is completely soluble in excess of caustic soda or potash solution, and in hydrochloric acid. The compound, when washed and dried, forms a hard mass which breaks with a conchoidal fracture and is of a bluish colour, probably due to decomposition.

Precipitated from the alkali metal ferrocyanides, the precipitate contains alkali metal in combination. The compounds $AlKFe(CN)_64H_2O$ and $AlNH_4Fe(CN)_64H_2O$

have been described:[1] they are prepared by adding aluminium chloride solution to potassium and ammonium ferrocyanide respectively. When anhydrous they are said to be of a blue colour.

AMMONIUM FERROCYANIDE, $(NH_4)_4Fe(CN)_6 4H_2O$, may be easily obtained by boiling the barium salt or the double ammonium barium salt with the equivalent quantity of ammonium sulphate and crystallizing the solution by rapid evaporation, preferably under a vacuum; or by precipitation with alcohol. It forms the double salts, $(NH_4)_4Fe(CN)_6 2NH_4Cl 3H_2O$ and $(NH_4)_4Fe(CN)_6 2NH_4Br 3H_2O$, in well-defined deep yellow crystals when solutions of the two salts are mixed in equivalent proportions. It also forms the soluble double ferrocyanides, $K_3NH_4Fe(CN)_6 3H_2O$, $(NH_4)_2K_2Fe(CN)_6 3H_2O$, and $Na_3NH_4Fe(CN)_6$; the sparingly soluble double salts, $Ca(NH_4)_2Fe(CN)_6$, $Ba(NH_4)_2Fe(CN)_6 3H_2O$, and $Mg(NH_4)_2Fe(CN)_6 H_2O$; and a number of insoluble double salts, such as $Cu(NH_4)_2Fe(CN)_6 H_2O$, $Co(NH_4)_2Fe(CN)_6 XH_2O$, $Fe''(NH_4)_2Fe(CN)_6 XH_2O$, etc.

The solution of ammonium ferrocyanide is exceedingly unstable, and rapidly decomposes on boiling, ammonium cyanide being evolved, and a dull green precipitate of ferrosoferric ammonium ferrocyanide formed:

$$14(NH_4)_4Fe(CN)_6 + O_2 = 2Fe'''_2Fe''(NH_4)_8[Fe(CN)_6]_4 + 36NH_4CN + 4NH_3 + 2H_2O.$$

When the dry salt is heated out of air contact a black magnetic powder is left, which is said to be iron carbide, FeC_2.[2]

The double compound with mercuric cyanide, $(NH_4)_4Fe(CN)_6 3Hg(CN)_2 2H_2O$, has been described by D. Strömholm.[3]

BARIUM FERROCYANIDE, $Ba_2Fe(CN)_6 6H_2O$, is readily prepared by adding a strong barium chloride

[1] Robinson, *J.C.S.*, **95**, 1353–59.

[2] N. Ljubavin, *J. Russ. Phys. Chem. Soc.* (1912), **44**, 609.

[3] *Z. anorg. Chem.* (1913), **84**, 208–16.

solution to a moderately strong solution of sodium ferrocyanide. The compound immediately separates out in the form of a light yellow, sparingly soluble, crystalline powder. It may also be prepared in a similar manner from strontium, magnesium or calcium ferrocyanide, but potassium ferrocyanide should not be used or the potassium double salt will be formed, which is only converted into the pure barium salt by repeated treatment with strong barium chloride solution.

The salt is very sparingly soluble in water. 100 c.c. of water at 15.5° C. will dissolve 0.34 grm. of the anhydrous salt and 1.01 grm. at 100° C. When digested in a solution of ammonium chloride the double salt, $Ba(NH_4)_2Fe(CN)_6 3H_2O$, is formed. This salt may also be obtained by precipitating sodium ferrocyanide solution containing an excess of ammonium chloride with barium chloride solution; it is a sparingly soluble crystalline salt, closely resembling the pure barium salt in appearance, but it retains all its combined water at 100° C. The potassium salt, $BaK_2Fe(CN)_6 3H_2O$, may be prepared in a similar manner, or by adding barium chloride solution, not in excess, to potassium ferrocyanide solution; it is a sparingly soluble crystalline precipitate which loses all combined water when heated to 100° C: 100 c.c. of water at 15.5 dissolve 2.1 grm. of the anhydrous potassium double salt, and 6.08 grm. at 100° C. No double sodium salt has been formed; the ammonium double salt is completely converted into the potassium compound by repeatedly digesting it with excess of potassium chloride solution, and vice versa.

BISMUTH FERROCYANIDE is obtained as a white precipitate, when produced from potassium ferrocyanide solution, the precipitate contains potassium in combination and is said to have the composition agreeing with the formula, $BiKFe(CN)_6 4H_2O$ (Wyrnbow). The precipitate, when warmed with nitric acid, is converted into bismuth ferricyanide.

CADMIUM FERROCYANIDE, $Cd_2Fe(CN)_6 7H_2O$, prepared from the calcium salt, is a white, somewhat gelatinous precipitate, which when washed and dried forms a soft white powder, unattacked by the boiling carbonates of the alkali metals, but dissolves to a clear solution in a strong solution of caustic soda or potash or in ammonia. When warmed with strong hydrochloric acid it is decomposed with formation of hydroferrocyanic acid, which is precipitated insoluble in the strong acid liquor. Boiled with strong nitric acid, it is converted into the corresponding insoluble ferricyanide. If cadmium chloride solution is added to a large excess of calcium ferrocyanide solution in the cold a white gelatinous precipitate is formed, having the composition $Cd_3Ca[Fe(CN)_6]_2 20H_2O$. Precipitates obtained from the alkali metal ferrocyanides by the addition of a soluble cadmium salt contain varying quantities of alkali metal in combination.

CAESIUM FERROCYANIDE, $Cs_4Fe(CN)_6 6H_2O$, may be prepared by decomposing the barium salt by boiling with a solution of caesium sulphate. The compound separates from its aqueous solutions in yellow crystals, which are very soluble in water.

CALCIUM FERROCYANIDE, $Ca_2Fe(CN)_6 12H_2O$. This salt is easily prepared by boiling the double calcium ammonium salt with an excess of lime, until all the ammonia is driven off, and then filtering and evaporating the liquor. This double salt is readily obtained by adding a mixture of calcium and ammonium chloride in equal molecular proportions to a moderately strong solution of sodium ferrocyanide :

$$Na_4Fe(CN)_6 + CaCl_2 + 2NH_4Cl = Ca(NH_4)_2Fe(CN)_6 + 4NaCl.$$

The double salt separates out in the cold in sparingly soluble white microscopic crystals, which is filtered and washed free from sodium chloride, and then boiled with an excess of milk of lime :

$$Ca(NH_4)_2Fe(CN)_6 + Ca(OH)_2 = Ca_2Fe(CN)_6 + 2NH_3 + 2H_2O.$$

Calcium ferrocyanide is a very soluble salt : the

evaporated solution when filtered forms a thick syrup, which exhibits the phenomena of supersaturation to a marked degree, the clear concentrated liquor remaining uncrystallized for a long time, but on stirring rapid crystallization takes place. By slow evaporation fine, large and well-formed crystals of a pale yellow colour can be easily obtained, containing twelve molecules of water. When heated to 100° C., 11 to 11½ molecules of water are readily given off and the remainder with difficulty. When, however, the salt is heated in a current of dry air all the water is given off.[1]

The salt is much less soluble in solutions of other calcium salts, such as the chloride or thiocyanate, than in pure water, and it is insoluble in alcohol. It forms the sparingly soluble double salt, $Ca(NH_4)_2Fe(CN)_6$, prepared as described above, or by adding a solution of ammonium chloride to the calcium ferrocyanide, which separates from the liquor in small anhydrous crystals. The corresponding potassium double salt, $CaK_2Fe(CN)_6$, may be prepared in a similar manner by adding a solution of a mixture of calcium and potassium chloride to a solution of sodium ferrocyanide ; and it may also be prepared by adding calcium chloride to a solution of potassium ferrocyanide. By whichever method it is prepared it separates from the solution in minute faintly yellow crystals, sparingly soluble in water. These crystals are anhydrous and are somewhat more soluble in water than the corresponding ammonium salt.

At 15° C. 100 c.c. of water dissolve 0.35 grm. of the ammonium salt, and 0.72 grm. of the potassium salt ; while at 100° C., 0.39 grm. and 0.8 grm. respectively are dissolved.

When a cold saturated solution of sodium chloride is added to a cold saturated solution of calcium ferrocyanide, small yellow crystals of the double calcium sodium ferrocyanide, $CaNa_2Fe(CN)_6 3H_2O$, separate out. This compound, unlike the double salts described above, is moderately soluble in water.

If a fairly concentrated solution of the calcium salt

[1] H. G. Coleman, *J. of Gas Lighting* (1910), 583.

is boiled with magnesium chloride, a white precipitate separates of a double calcium magnesium ferrocyanide, $Ca_2Mg_4[Fe(CN)_6]_3 24H_2O$. This salt is very soluble in pure water with decomposition, and it loses one-third of its combined water at 100° C. Calcium ferrocyanide also combined with free lime, and some basic salts are known.

Heavy metal ferrocyanides produced by direct precipitation of the calcium ferrocyanide solution seldom contain calcium in combination, particularly if an excess of the heavy metal solution is used, and this fact may be made use of as a general method for the preparation of pure heavy metal ferrocyanides. In certain cases, however, and in the presence of a large excess of calcium ferrocyanide, double calcium and heavy metal ferrocyanides may be obtained, *e.g.* $Cd_3Ca[Fe(CN)_6]_2$, $CuCaFe(CN)_6$, etc.

Dry calcium ferrocyanide, when heated out of air contact, decomposes with formation of calcium cyanamide, free carbon, and nitrogen, metallic iron, or iron carbide, thus :

$$Ca_2Fe(CN)_6 = 2CaCN_2 + Fe + N_2 + 4C,$$

no calcium cyanide being formed.

CERIUM FERROCYANIDE, $Ce_4[Fe(CN)_6]_3 30H_2O$, is obtained in the pure state when the calcium salt solution is precipitated with cerous chloride. The precipitate which at first forms is white and voluminous, but it rapidly changes to a coarse crystalline powder. If alkali metal ferrocyanides are used in place of the calcium salt, white bulky precipitates of varying composition are formed, containing the alkali metal in combination. In this manner the compounds, $CeKFe(CN)_6 4H_2O$; $CeNaFe(CN)_6$, and $CeNH_4Fe(CN)_6$, have been prepared.

CHROMIUM FERROCYANIDE. The addition of a chromic salt to a soluble ferrocyanide produces no precipitate, but when the solution is heated, hydrocyanic acid is evolved and the mass sets to a greenish-brown jelly, which when washed and dried yields a dark brown, almost black, vitreous mass.

COBALT FERROCYANIDE, $Co_2Fe(CN)_6 9H_2O$, is obtained as a fine green precipitate by the precipitation of a solution of the calcium or hydrogen salt with cobalt chloride. The precipitate is insoluble in water or dilute acids, but is decomposed by the carbonates or hydroxides of sodium or potassium, and is entirely soluble in ammonia and ammonium carbonate.

If the cobaltous salt is added to a large excess of the calcium salt, a double cobaltous calcic ferrocyanide is obtained as a green precipitate, which when washed and air-dried has the composition represented by the formula $Co_3Ca[Fe(CN)_6]_2 14H_2O$. At 100° C. seven molecules of water are driven off. In a similar manner the compounds, $Co_3Sr[Fe(CN)_6]_2$; $Co_3Mg[Fe(CN)_6]_2$, and $Co_3L_2[Fe(CN)_6]_2$, may be prepared.

By precipitating an alkali metal ferrocyanide with a solution of a cobalt salt, a very large number of complex compounds can be produced containing the alkali metal in combination. The double salt, $CoK_2Fe(CN)_6$, is obtained as a light dirty green precipitate in a very fine state of division, and difficult to filter, when the cobalt salt is added to a large excess of potassium ferrocyanide solution, preferably in the presence of an excess of potassium chloride. The compound, $Co(NH_4)_2Fe(CN)_6$, may also be prepared by substituting ammonium ferrocyanide and chloride for the potassium salts. This precipitate is also of a dirty green colour. Magnesium ferrocyanide exactly precipitated by a cobalt salt solution precipitates the compound, $Co_3Mg[Fe(CN)_6]_2$, and if the precipitation takes place in the presence of a large excess of magnesium chloride, a compound agreeing with the formula, $Co_4Mg_2[Fe(CN)_6]_3$, is obtained. Potassium ferrocyanide solution, when exactly precipitated by a cobalt salt, or vice versa, yields a dirty greenish precipitate of the composition, $Co_6K_8[Fe(CN)_6]_5 35H_2O$, which loses twenty molecules of water at 100° C. The compound, $Co_4Na_4[Fe(CN)_6]_3$, is obtained by precipitating sodium ferrocyanide in presence of an excess of sodium chloride with a cobaltous salt.

The dry cobalt ferrocyanides, when digested in concentrated hydrochloric acid, are decomposed, the whole of the cobalt passing into solution in the acid and hydroferrocyanic acid, which remains insoluble. If, however, the acid is diluted with twice its volume of water, and the cobalt ferrocyanide digested in it, in a warm place, half of the metallic base is replaced by hydrogen. If the acid is filtered off and the compound washed and dried it is obtained as a dark blue powder of the composition, $CoH_2Fe(CN)_6 4H_2O$, which is quite stable in the dry state, but is decomposed with evolution of hydrocyanic acid, or boiling with water. When treated with alkaline carbonates the hydrogen is replaced with effervescence.

COPPER FERROCYANIDES — CUPRIC FERROCYANIDES. The addition of a cupric salt solution to a solution of a ferrocyanide forms a precipitate of a reddish-brown colour varying in tint and composition according to the conditions of the precipitation, and to the particular ferrocyanide used. If the solutions are dilute the precipitate separates in thick gelatinous flocks, but if concentrated the mass sets to a stiff jelly.

Pure cupric ferrocyanide, $Cu_2Fe(CN)_6 11H_2O$, can only be prepared by adding calcium ferrocyanide or hydroferrocyanic acid solution to an excess of cupric chloride solution, or by dissolving cupric carbonate or hydroxide in the dilute acid.

A large number of double salts of the type $CuM'_2Fe(CN)_6$ and $CuM''Fe(CN)_6$ are known, *e.g.* cupric ammonium ferrocyanide, $Cu(NH_4)_2Fe(CN)_6H_2O$, prepared by adding a cupric salt to a large excess of ammonium ferrocyanide solution containing ammonium chloride. It is a dense red-brown powder which retains the one molecule of water at 100° C. Cupric calcium ferrocyanide, $CuCaFe(CN)_6 12H_2O$, is obtained by adding cupric chloride solution to a large excess of the calcium salt. It forms, when washed and dried, a rather light brown loose powder, which when heated to 100° C. loses eight molecules of water, and changes

in colour from light brown to a magnificent violet. On subsequent exposure to moist air the eight molecules of water are slowly reabsorbed, the colour passing back from violet to the original light brown.[1] The magnesium salt, $CuMgFe(CN)_6 10H_2O$, is obtained by the addition of the cupric salt to a solution containing excess of both magnesium ferrocyanide and chloride: the washed and dried precipitate forms a hard dark brown mass. The cupric potassium salt, $[CuK_2Fe(CN)_6]_2H_2O$, is obtained as a very dense, red-brown, granular powder by adding the cupric salt to an excess of potassium ferrocyanide and chloride solution.

The cupric sodium salt, $CuNa_2Fe(CN)_6 3H_2O$, is obtained as a reddish-brown powder by adding the cupric salt to a large excess of sodium ferrocyanide, which loses one molecule of water at 100° C. A compound of the same composition, but in the form of a loose light brown powder, may be prepared by digesting freshly precipitated cupric carbonate in an excess of sodium ferrocyanide solution for some time with repeated agitation. Cupric strontium ferrocyanide, $CuSrFe(CN)_6 10H_2O$, obtained from excess of strontium ferrocyanide solution and a cupric salt, forms, when washed and dried, a very dense body of a dark brown almost black colour, which when heated to 100° C. loses seven molecules of water, all of which is exactly reabsorbed on subsequent exposure to the air. Cupric hydrogen ferrocyanide, $CuH_2Fe(CN)_6 4H_2O$, may be prepared by boiling any cupric ferrocyanide with strong hydrochloric acid, and washing the precipitate with strong acid and finally with water or alcohol. It is obtained when dry as a yellow powder, which is quite stable in the dry state, but decomposed by boiling with water, hydrocyanic acid being evolved. Cupric lithium ferrocyanide has been prepared[2] by boiling cupric ferrocyanide free from alkali metal, with lithium ferrocyanide solution, in quadratic red plates or brownish-red needles.

[1] H. E. Williams. *Chem. World*, 1, 43.

[2] Messner, *Z. anorg. Chem.* (1895–99), 126–43.

A very large number of other double ferrocyanides of copper may be prepared, which may be considered as molecular compounds of the double salts, $CuM''Fe(CN)_6$ or $CuM'_2Fe(CN)_4$, with pure cupric ferrocyanide, $Cu_2Fe(CN)_6$, of the general formula, $XCuM'_2Fe(CN)_6 + YCu_2Fe(CN)_6$, for the alkali metal compounds; and $XCuM''Fe(CN)_6 + YCu_2Fe(CN)_6$, for the alkaline earth metal compounds.

Compounds of the type, $Cu_3M'_2[Fe(CN)_6]_2$ or $Cu_3M''[Fe(CN)_6]_2 = Cu_2Fe(CN)_6 : CuM''(orM'_2)Fe(CN)_6$. When pure magnesium ferrocyanide is exactly precipitated with sulphate of copper solution, the washed and dried precipitate has the composition $Cu_3Mg[Fe(CN)_6]_2$-$20H_2O$, and is of a dark brown colour. The sodium compound, $Cu_3Na_2[Fe(CN)_6]_2$, may be prepared in an exactly similar manner: the same compound is also formed when a solution of a copper salt is exactly precipitated with sodium ferrocyanide.

Compounds of the type, $Cu_4M'_4(or\ M''_2)[Fe(CN)_6]_3 = Cu_2Fe(CN)_6 : 2CuM'_2(or\ M'')Fe(CN)_6$. The magnesium compound, $Cu_4Mg_2[Fe(CN)_6]_330H_2O$, is obtained when magnesium ferrocyanide solution containing a large excess of magnesium chloride is exactly precipitated with a solution of a cupric salt: the compound when dry forms hard dark brown masses, which lose twenty molecules of water at 100° C. The potassium compound, $Cu_4K_4[Fe(CN)_6]_3XH_2O$, is obtained whenever a solution of potassium ferrocyanide free from other potassium salts is precipitated exactly with a cupric salt.

Compounds of the type, $Cu_6M'_8(or\ M''_4)[Fe(CN)_6]_5 = Cu_2Fe(CN)_6 ; 4CuM'_2(or\ M'')Fe(CN)_6$. The ammonium salt of this type is always formed when pure ammonium ferrocyanide is exactly precipitated by a cupric salt, $Cu_6(NH_4)_8[Fe(CN)_6]_5$; and the potassium compound, $Cu_6K_8[Fe(CN)_6]_5XH_2O$, when potassium ferrocyanide containing a large excess of potassium chloride is exactly precipitated with a copper salt; it is also always formed when any soluble ferrocyanide, with the exception of the ammonium salt, is exactly precipitated

with a cupric salt solution in the presence of a large excess of potassium chloride.

Compounds of the type, $Cu_7M'_6$(or M''_3)$[Fe(CN)_6]_5 = 2Cu_2Fe(CN)_6 : 3CuM'_2Fe(CN)_6$. When sodium ferrocyanide solution containing sodium chloride is exactly precipitated with a cupric salt, a compound of the above type is obtained, $Cu_7Na_6[Fe(CN)_6]_5 50H_2O$. The potassium salt, $Cu_7K_6[Fe(CN)_6]_5 22H_2O$, is produced when an excess of the copper salt is added to a solution of potassium ferrocyanide containing potassium chloride.

When a solution of a cupric salt is added to pure ammonium ferrocyanide, the latter being in large excess and free from other ammonium salts, a compound is obtained of the composition, $Cu_7(NH_4)_{10}[Fe(CN)_6]_6$, which loses sixteen molecules of water at 100° C. The same compound is also obtained by exactly precipitating a solution of the ferrocyanide containing a large excess of ammonium chloride with the copper salt. The corresponding potassium compound is formed by adding the copper salt to a large excess of potassium ferrocyanide free from other potassium salts, $Cu_7K_{10}[Fe(CN)_6]_6 48H_2O$, which retains twelve molecules of water at 100° C.

When a large excess of the copper salt is used to precipitate the alkali metal ferrocyanides, the precipitates still always contain some alkali metal in combination. Thus when the ammonium salt is precipitated with excess of sulphate of copper, the precipitate has the composition $Cu_5(NH_4)_2[Fe(CN)_6]_3 28H_2O = Cu(NH_4)_2Fe(CN)_6 : 2Cu_2Fe(CN)_6$; and the potassium salt prepared under similar conditions has the composition $Cu_9K_2[Fe(CN)_6]_5 50H_2O = CuK_2Fe(CN)_6 : 4Cu_2Fe(CN)_6$, which retains fifteen molecules of water at 100° C.; while the sodium salt has the composition $Cu_{11}Na_2[Fe(CN)_6]_6 54H_2O = CuNa_2Fe(CN)_6 : 5Cu_2Fe(CN)_6$.

When a ferrocyanide solution is added to an ammoniacal solution of a cupric salt, a precipitate is formed after a short time, small yellowish-brown silky crystals being deposited of the additive compound, $Cu_2Fe(CN)_6 4NH_3H_2O$, insoluble in water. The com-

pound is fairly stable and can be dried in the air without loss of ammonia. If a solution of a cupric salt is added to a solution of ammonium ferrocyanide containing a very large excess of ammonia, and the mixture allowed to stand some hours, beautiful black lustrous prisms are obtained which are sparingly soluble in ammonia, and which quickly decompose, giving off ammonia on exposure to the air.

When freshly precipitated cupric ferrocyanide is warmed on the water-bath to 60° to 70° C., with an excess of a strong solution of sodium carbonate, the red-brown colour of the copper ferrocyanide changes to a bright green, with the formation of a basic compound having the composition agreeing with the formula $CuNa_2Fe(CN)_6CuO8H_2O$:

$$Cu_2Fe(CN)_6 + Na_2CO_3 = CuNa_2Fe(CN)_6CuO + CO_2$$

if the temperature is allowed to rise above 80° C. decomposition occurs, first forming cupric carbonate, then black cupric oxide, sodium ferrocyanide passing into solution. A similar potassium compound may be prepared, but attempts to prepare the corresponding ammonium compound in a similar manner failed, the copper ferrocyanide being converted by the ammonium carbonate into the red double salt, $Cu(NH_4)_2Fe(CN)_6$.

When precipitated and washed cupric ferrocyanide is boiled with a strong solution of potassium thiocyanate, the brown colour of the ferrocyanide changes to the blue ferric cupric ferrocyanide, while cyanogen is evolved and a double cuprocyanide and cuprous thiocyanate of potassium remain in solution. The cuprous thiocyanate may be precipitated by diluting the filtrate. This reaction proceeds as follows :

$$8Cu_2Fe(CN)_6 + 7KCNS = 2Fe'''_2Cu'[Fe(CN)_6]_2 + 7Cu'K(CN)_2 + 7Cu'CNS + 5(CN)_2$$

If the copper ferrocyanide precipitate is added to a large excess of a strong solution of an alkali metal ferrocyanide and gently warmed, the precipitate dissolves, but separates out on cooling, as the double salt, $CuM'_2Fe(CN)_6$, where M is (Na, K, NH_4, etc.,)

according to the ferrocyanide used. If, however, the solution is boiled for some time a blue precipitate is deposited with evolution of cyanogen, and a double cuprocyanide is formed in solution.

Chlorine gas passed through a suspension of freshly prepared cupric ferrocyanide completely converts it into the green cupric ferricyanide. By boiling the dry and powdered cupric ferrocyanide with strong nitric acid until all action ceases, a dark brown powder is obtained, which when washed and dried has a composition agreeing with the formula, $Cu_5[Fe(CN)_6]_3 27H_2O$; this compound contains both ferro-and ferricyanide in the proportion of 1 : 2 and is a cupric ferroferricyanide :

$$Cu_5[Fe(CN)_6]_3 = Cu_3[Fe'''(CN)_6]_2 : Cu_2Fe''(CN)_6 = Cu_5[Fe''Fe'''_2(CN)_{18}].$$

By boiling cupric ferrocyanide with an excess of a solution of ferric chloride, a part of the copper is replaced by ferric iron, and a blue compound of the composition $Fe'''_2Cu''[Fe(CN)_6]_2 28H_2O$ results.

CUPROUS FERROCYANIDE. When a solution of cuprous chloride in hydrochloric acid or calcium chloride is added to a solution of calcium ferrocyanide or hydroferrocyanic acid, a white precipitate results of cuprous ferrocyanide, $Cu'_4Fe(CN)_6XH_2O$, which rapidly oxidizes in the air to the cupric compound, and it is completely decomposed by boiling with dilute sulphuric or hydrochloric acid.

A number of double cuprous ferrocyanides are known, and are prepared by adding cuprous chloride to an excess of a soluble ferrocyanide. The cuprous chloride is dissolved in the chloride of the base of the ferrocyanide taken, and added to a large excess of the ferrocyanide. The mixture is gently warmed and filtered, when the double salt crystallizes out on cooling in colourless six-sided prisms. They may also be obtained by boiling the corresponding ferrocyanide with cuprous cyanide. The mixture must not, however, be boiled or kept heated for any length of time or a further and more deep-seated reaction will take

place and a double ferrous ferrocyanide will be precipitated:

$$K_4Fe(CN)_6 + 4CuCN = Cu'_2K_2Fe(CN)_6 + 2CuK(CN)_2.$$
$$K_4Fe(CN)_6 + 2CuCl = Cu'_2K_2Fe(CN)_6 + 2KCl.$$

The double cuprous ferrocyanides of sodium, potassium, ammonium, lithium, calcium, barium, and strontium, have been prepared and described by J. Messner,[1] and are said to be all similar in appearance and crystalline form.

These compounds are slowly oxidized in the moist state, but when dry may be kept some time without oxidation. They are completely decomposed when boiled with dilute hydrochloric acid, and also by dilute sulphuric acid in the presence of a small quantity of a chloride.

HYDROFERROCYANIC ACID, $H_4Fe(CN)_6$, may be obtained in solution pure by adding the calculated quantity of sulphuric acid to barium or lead ferrocyanide suspended in water. It may also be obtained in the crystalline form by the addition of the theoretical quantity of hydrochloric acid to a moderately strong solution of sodium or potassium ferrocyanide dissolved in air-free water; by shaking the solution with a little ether crystals of the acid separate out. If to a strong solution of a ferrocyanide an excess of concentrated hydrochloric acid is added, a white precipitate is formed consisting of minute crystals of hydroferrocyanic acid, which may be washed first with hydrochloric acid to remove the alkali metal chloride and finally with a mixture of alcohol and ether. The acid may be purified by first dissolving it in alcohol and then reprecipitating the acid by the addition of ether.

Hydroferrocyanic acid crystallizes from water in colourless scales. It is very soluble in water and alcohol, but is insoluble in ether, and may be made to crystallize from its aqueous solutions by the addition of ether. It is a strong tetrabasic acid, the aqueous solutions give a strong acid reaction with indicators,

[1] *Z. anorg. Chem.*, **8**, 368–93.

and decompose the alkaline carbonates with effervescence.

It is stable in the dry state at the ordinary temperature, but in solution it evolves a small quantity of hydrocyanic acid and gradually deposits an increasing precipitate of a ferric ferrocyanide. It is stated [1] that when a solution of hydroferrocyanic acid is boiled, half of the cyanogen is evolved as hydrocyanic acid, the remainder being precipitated as a bluish white precipitate of ferrous hydrogen ferrocyanide :

$$2H_4Fe(CN)_6 = Fe''H_2Fe(CN)_6 + 6HCN.$$

This, however, does not seem to be the case, no acid ferrocyanide being formed, two-thirds of the total cyanogen being readily obtained on boiling the solution, as hydrocyanic acid, and the remainder as the insoluble ferrous ferrocyanide, thus :

$$3H_4Fe(CN)_6 = Fe''_2Fe(CN)_6 + 12HCN.$$

When the dry ferrocyanides of lead, cadmium or zinc are digested with strong hydrochloric acid, a white insoluble matter remains, consisting of pure hydroferrocyanic acid. If, however, the cupric ferrocyanide is boiled with strong hydrochloric acid, only half of the copper passes into solution, the brown colour of the copper ferrocyanide changes to greenish-yellow. The insoluble compound remaining may be filtered off and washed with water and dried. This compound is a cupric hydrogen ferrocyanide with a composition agreeing with the formula, $CuH_2Fe(CN)_64H_2O$. It may also be prepared by boiling ground sodium or potassium ferrocyanide and half the equivalent of ground sulphate of copper, with an excess of strong hydrochloric acid.

The air-dried compound is a greenish-yellow powder which is insoluble in water, and decomposes alkaline carbonates with effervescence. When digested with a solution of an alkali metal chloride the hydrogen is replaced by the alkali metal, and hydrochloric acid is

[1] Reimann and Carum, *A.*, **113**, 39.

liberated; potassium or ammonium chloride liberate two equivalents of hydrochloric acid, forming the red-brown double salt, thus:

$$CuH_2Fe(CN)_6 + 2KCl = CuK_2Fe(CN)_6 + 2HCl.$$

The action of sodium chloride is, however, somewhat different, only one equivalent of hydrogen being replaced, and a dull brown finely divided precipitate of the triple salt, $CuNaHFe(CN)_6$, remains. The remaining hydrogen atom may be replaced by the addition of potassium chloride solution, the colour of the compound then changing to red-brown with formation of the compound, $CuNaKFe(CN)_6$, and liberation of hydrochloric acid.

The cupric hydrogen ferrocyanide, although quite stable in the boiling strong hydrochloric acid, is decomposed when boiled with water, hydrocyanic acid being evolved, and a mixture of cupric and ferrous ferrocyanides being precipitated.

By using a diluted hydrochloric acid other insoluble acid salts may be prepared, and by this means the following compounds have been obtained. Cobalt hydrogen ferrocyanide, $CoH_2Fe(CN)_6 4H_2O$, as a bright blue powder, insoluble in water; nickel hydrogen ferrocyanide, $NiH_2Fe(CN)_6 3H_2O$ as a loose, light green powder, and manganese hydrogen ferrocyanide, $MnH_2Fe(CN)_6 5H_2O$, is obtained as a white insoluble powder.[1]

Like the copper salt these compounds yield the whole of their hydrogen in the form of hydrochloric acid when digested with ammonium or potassium chloride, but differ from that compound in their action with sodium chloride. They are all quite stable in the dry state, but are decomposed when boiled with water, and also decompose alkaline carbonates with effervescence.

The sparingly soluble ferrocyanides formed by the organic ammonias in acid solutions are also double hydrogen compounds, thus the addition of diethyl-

[1] H. E. Williams, *P.C.S.*, **28**, 407, 317.

aniline hydrochloride solution containing an excess of hydrochloric acid to a solution of a ferrocyanide precipitates the compound diethylaniline hydrogen ferrocyanide, $[C_6H_5N(C_2H_5)_2H]_2H_2Fe(CN)_6 8H_2O$, in small pale yellow needles; in a similar manner the dimethylaniline hydrogen salt, $[C_6H_5N(CH_3)_2H]_2H_2Fe(CN)_6 4H_2O$; the monomethylaniline hydrogen salt, $[C_6H_5NHCH_3H]H_2Fe(CN)_6 4H_2O$; and the pyridine salt, $(C_5H_5NH)_2H_2Fe(CN)_6 2H_2O$, may be prepared. They are all sparingly soluble in water, and separate out from solution in small pale yellow crystals, which are decomposed by boiling with water.[1]

THE FERROCYANIDES OF IRON — FERRIC FERROCYANIDES. When a ferric salt is added to a solution of a ferrocyanide, a deep blue bulky precipitate is obtained, which varies in composition and properties according to the method of preparation and to the particular ferrocyanide used. The exact nature and constitution of these precipitates is still the subject of much discussion.

Pure ferric ferrocyanide corresponding to the formula $Fe'''_4[Fe''(CN)_6]_3 XH_2O$ is, however, only obtained when a solution of pure hydroferrocyanic acid or calcium ferrocyanide is added to an excess of an acidified solution of a ferric salt. When the precipitation takes place in neutral solutions the blue precipitate is liable to carry down with it some ferric hydroxide.

The blue so obtained, when washed and air-dried, contains a very considerable proportion of water of hydration, or constitution very firmly combined, the greater portion of which is retained when the compound is heated to 100° C. If the heating is continued above this temperature a further quantity of the water may be driven off, but it is impossible to remove all the combined water without the blue decomposing, hydrocyanic acid, together with other compounds, being evolved, leaving a residue of ferric oxide, if the heating takes place in air contact. Anhydrous ferric ferrocyanide has not yet been obtained.

[1] H. E. Williams, *l.c.*

Pure ferric ferrocyanide cannot be obtained by the precipitation of an alkali metal ferrocyanide by a ferric salt, as the product, even when most carefully prepared and washed, always contains some of the alkali metal in combination. When the iron salt is added to a large excess of an alkali metal ferrocyanide such as a solution of the potassium salt, a blue ferric potassium ferrocyanide is obtained of a composition agreeing with the formula $Fe'''KFe''(CN)_6$. This compound, known as soluble blue, forms a colloidal solution with water, and has been shown, by the researches of K. A. Hofmann and others, to be identical in composition and properties to the blue precipitate obtained by the addition of a ferrous salt to an excess of potassium ferricyanide.

When ammonium ferrocyanide solution in excess is precipitated by an iron salt in the same manner, a blue compound, $Fe'''NH_4Fe''(CN)_6$, of similar composition and properties, is obtained; but no compound corresponding to the formula $Fe'''NaFe''(Cn)_6$ has as yet been prepared, but if ferric chloride solution is added to a large excess of sodium ferrocyanide solution containing an equivalent quantity of ammonium sulphate or chloride, a soluble blue is obtained of the composition agreeing with the formula, $Fe'''_6(NH_4)_5Na[Fe''(CN)_6]_6 33H_2O = 5FeNH_4Fe(CN)_6 \cdot FeNaFe(CN)_6$.

It is usually assumed that blue compounds containing alkali metal between the limits of the formulæ, $FeM'Fe(CN)_6$ and $Fe_4[Fe(CN)_6]_3$, are mere mixtures of these two compounds. It is, of course, true that in many cases the precipitate is a mere mechanical mixture of one or more compounds.

A number of blue compounds have been prepared by the author[1] under definite conditions, the analysis and examination of which leave no doubt that a very great number of blue compounds of constant composition may be prepared.

Of these compounds those prepared from potassium or ammonium ferrocyanide usually show great

[1] H. E. Williams, *J.C.M.M.S. of S. Africa*, **15**, 1

similarity in composition and appearance, and those of similar composition are obtained under similar conditions; whereas the blues prepared from sodium ferrocyanide usually contain a smaller proportion of alkali metal in combination than when the ammonium or potassium salt is used, and the precipitates also differ greatly in appearance, the dried blues being generally much less dense and of a lighter shade of blue, approaching ultramarine, and contain a greater proportion of combined water. They are also usually free, or almost free, from bronze lustre.

If a large excess of ammonium ferrocyanide solution is added to an ammoniacal solution of ferric tartrate, or citrate containing a considerable amount of ammonium tartrate or citrate and free ammonia, a dark brown solution is obtained. If now a mineral acid such as hydrochloric or dilute sulphuric acid is gradually added with agitation in sufficient proportions to neutralize the free ammonia and maintain an acidity due to the organic acid, a very finely divided bright-green precipitate is obtained, which must first be washed by decantation several times, then filtered and thoroughly washed.

The green compound so prepared, when carefully and completely washed and air-dried, has a composition agreeing with the formula $Fe'''_2(NH_4)_6[Fe''(CN)_6]_3 \cdot 27H_2O$, and is the true double ferric ammonium ferrocyanide in which exactly half of the basic iron of ferric ferrocyanide is replaced by ammonium:

$$2Fe'''_2(NH_4)_6[Fe''(CN_6)] = Fe'''_4[Fe''(CN)_6]_3 : 3(NH_4)_4Fe(CN)_6$$

This compound forms a green colloidal solution with water.

If to the freshly precipitated green compound prepared as described above a further quantity of mineral acid is added until a slight excess of free mineral acid, as well as the organic acid, exists in solution, the green compound changes to blue. This compound, which may be more readily washed, has, when air-dried, a composition agreeing with the formula,

$(Fe'''_3)(NH_4)_{12}[Fe(CN)_6]_652H_2O$, which may be considered as a compound of two molecules of the green ferric ammonium ferrocyanide described above, and one molecule of ferric ferrocyanide, thus:

$$Fe'''_8(NH_4)_{12}[Fe''(CN)_6]_9 = 2Fe'''_2(NH_4)_6[Fe''(CN)_6]_3 + Fe'''_4[Fe''(CN)_6]_3.$$

If in the preparation of the green salt potassium hydroxide and potassium ferrocyanide, etc., are substituted for the ammonia and ammonium salts, a green potassium compound is obtained when the alkaline solution is acidified with an organic acid, but the colour changes to a dull blue on washing. The compound, when thoroughly washed and dried, then has a composition:

$$Fe'''_{10}K_{18}[Fe''(CN)_6]_{12} = Fe'''_4[Fe''(CN)_6]_3 + 3Fe'''_2K_6[Fe''(CN)_6]_3.$$

When the compound is precipitated in the presence of free mineral acid, a blue of the composition $Fe'''_8K_{12}[Fe''(CN)_6]_9$ may be obtained.

Attempts to make similar sodium compounds did not succeed.

When solutions of the ferrocyanides are precipitated with a ferric salt a number of blue compounds of definite composition may be obtained, thus:

Blues of the type

$$Fe'''_7M'_3[Fe''(CN)_6]_6 = Fe'''_4[Fe''(CN)_6]_3 + 3Fe'''MFe''(CN)_6.$$

When sodium ferrocyanide solution is exactly precipitated by a ferrous salt, a bluish-white bulky precipitate is formed of ferrous sodium ferrocyanide. If an excess of ferric chloride solution is then added, and the mixture well agitated, the white precipitate is immediately coloured deep blue and a ferrous salt appears in solution. This blue precipitate, when thoroughly washed and air-dried, has a composition represented by the formula, $Fe'''_7Na_3[Fe(CN)_6]_650H_2O$, and the two reactions may be represented, thus:

(1) $Na_4Fe''(CN)_6 + Fe''SO_4 = Fe''Na_2Fe''(CN)_6 + Na_2SO_4$.

(2) $6Fe''Na_2Fe''(CN)_6 + 7Fe'''Cl_3 = Fe'''_7Na_3[Fe''(CN)_6]_6 + 6Fe''Cl_2 + 9NaCl$.

A blue having the same composition as the above, but with less combined water, may be obtained by treating with an excess of ferric chloride solution, while still boiling, the white ferrous sodium ferrocyanide precipitated by distilling sodium ferrocyanide with a dilute mineral acid: $Fe'''_7Na_3[Fe''(CN)_6]_6 24H_2O$.

The compound, $Fe_7(NH_4)_3[Fe(CN)_6]_6 50H_2O$, may be obtained by precipitating pure ammonium ferrocyanide solution with an excess of a solution of ferric chloride. Heated to 100° C., twenty-five molecules of water are evolved. A compound of the same composition may also be obtained by treating ferrous ammonium ferrocyanide with an excess of ferric chloride solution.

The compound, $Fe'''_7(NH_4)_2K[Fe(CN)_6]_6 42H_2O$, is precipitated by the addition of ferric chloride solution to potassium ferrocyanide, containing an excess of an ammonium salt. When heated to 100° C. the dried compound loses water equivalent to seventeen molecules.

Compounds of the type $Fe'''_{11}M'_3[Fe''(CN)_6]_9 = 2Fe'''_4[Fe''(CN)_6]_3 + 3Fe'''M'Fe''(CN)_6$.

When potassium ferrocyanide solution is precipitated with a slight but permanent excess of a ferric salt a blue is obtained of the composition, $Fe'''_{11}K_3[Fe''(CN)_6]_9 100H_2O$, which loses thirty-five molecules of water, when heated to 100° C. A compound of the same composition, but containing eighty-one equivalents of water, may be prepared by first precipitating the potassium salt solution with ferrous sulphate, and then adding an excess of ferric chloride to the precipitated ferrous potassic ferrocyanide and thoroughly agitating the mixture. The corresponding sodium salt may be obtained by oxidizing ferrous sodium ferrocyanide with chromic acid, $Fe_{11}Na_3[Fe(CN)_6]_9 90H_2O$.

If potassium ferrocyanide solution is added to a boiling excess of ferric chloride solution, a blue is obtained containing much less combined potassium than those described above, and having a composition agreeing with the formula, $Fe_9K[Fe(CN)_6]_7 78H_2O = FeKFe(CN)_6 : 2Fe_4[Fe(CN)_6]_3$; heated to 100° C. the

compound retains 49 molecules of water. If in the boiling iron solution a large amount of potassium chloride is dissolved before the addition of the ferrocyanide solution, a blue compound of the composition :

$$Fe'''_5K[Fe''(CN)_6]_{44}0H_2O = Fe'''KFe''(CN)_6 : Fe'''_4[Fe''(CN)_6]_3.$$

This compound loses 12 molecules of water at 100° C. The compound, $Fe_9Na[Fe(CN)_6]_7 70H_2O$, is obtained when freshly precipitated ferrous sodium ferrocyanide is oxidized by dilute nitric acid in the cold.

When sodium ferrocyanide is added to a boiling solution of ferric chloride, a blue of the composition $Fe'''_{13}Na[Fe''(CN)_6]_{10}124H_2O$ is formed = $Fe'''NaFe''(CN)_6 : 3Fe'''_4[Fe''(CN)_6]_3$. A compound of the same composition, but with 100 equivalents of water, may be obtained by precipitating sodium ferrocyanide solution with a large excess of a ferric salt. At 100° C., 80 equivalents of water are retained.

If the sodium ferrocyanide solution is saturated with an excess of ammonium sulphate or chloride, and then precipitated with a slight excess of ferric chloride, a blue precipitate is formed, the composition of which agrees with the apparently complex formula, $Fe_{22}(NH_4)_9Na[Fe(CN)_6]_{19}$, which may be considered as a complex molecule built up as follows :

(1) $FeNaFe(CN)_6 : 3Fe_7(NH_4)_3[Fe(CN)_6]_6$;

or

(2) $9Fe(NH_4)Fe(CN)_6 : Fe_{13}Na[Fe(CN)_6]_{10}$;

or

(3) $9Fe(NH_4)Fe(CN)_6 : FeNaFe(CN)_6 : 3Fe_4[Fe(CN)_6]_3$.

These blue compounds, when suspended in water and treated with chlorine, or when the dry compound is boiled with strong nitric acid, are converted into green ferric ferroferricyanides, several of which have been described under metallic ferricyanides.

The ferric ferrocyanides are readily decomposed by the hydroxides of the alkali and alkaline earth metals, and more slowly by the carbonates of the alkalis, but are practically unaffected by the action of cold aqueous

mineral acids. Concentrated sulphuric acid converts them into a white pasty mass of ferric sulphate and hydroferrocyanic acid, from which the original blue may be regenerated by treatment with water. Strong hydrochloric acid decomposes them into ferric chloride and hydroferrocyanic acid, the latter of which decomposes, but at a much slower rate than when this acid is boiled with distilled water. If the clear acid solution is allowed to evaporate spontaneously, lustrous crystals of prussian blue may be obtained.[1] When the prussian blue is boiled with a mixture of hydrochloric acid and alcohol, a larger proportion of the blue is dissolved forming a colourless solution, and the amount dissolved increases with the molecular weight of the alcohol used. On dilution the blue is precipitated.

Several of the blues are soluble in solutions of oxalic acid or ammonium tartrate, forming deep blue solutions. A blue ink was at one time made in this manner.

The ferric ferrocyanides are tasteless and odourless bodies of a deep blue colour, varying a little in shade according to the method of preparation, many of which exhibit a strong coppery lustre in the dry state.

FERROUS FERROCYANIDE. When a ferrous salt is added to a solution of a ferrocyanide, a white voluminous precipitate is immediately formed, which, unless the solutions are moderately dilute, sets to a thick gelatinous magma. This white precipitate rapidly absorbs oxygen from the air and turns a deep blue, with formation of ferric ferrocyanide. This action is so rapid that it is difficult to prepare ferrous ferrocyanide quite free from blue tinge. The precipitates obtained from the alkali metal salts contain a large proportion of alkali metal in combination generally amounting to half the total base. When prepared from the alkaline earth metal ferrocyanides, however, with the exception of magnesium, the precipitate generally consists of pure ferrous ferrocyanide free from other base.

The ferrous ferrocyanides, when treated with nitric

[1] Gintl, *D.P.J.*, **835**, 248.

acid or other oxidizing agents and warmed, are oxidized with the formation of fine blue compounds. These blues differ from the ordinary ferric ferrocyanides produced by the precipitation of a ferrocyanide with a ferric salt, in that on treatment with alkali several of them are decomposed into a ferrocyanide and ferrosoferric hydroxide, and also that when the washed blue is shaken up with a solution of a ferrocyanide, the blue insoluble matter changes more or less to white with the reformation of ferrous ferrocyanide, while some ferricyanide appears in solution. These blues are probably ferrous ferricyanides.

Ferrous ferrocyanides are not decomposed by boiling with a solution of the alkaline carbonates, but on the other hand they are completely decomposed by treatment with a slight excess of a solution of the caustic alkalis.

When treated with an excess of a cupric salt solution the ferrous ferrocyanides are converted into blue compounds which, however, differ from the blue compounds described above as they contain copper in combination. The reaction with ferrous sodium ferrocyanide may be represented thus :

$$12Fe''Na_2Fe''(CN)_6 + 12CuSO_4 = 2Fe'''_5Cu'_6Na_3(Fe''(CN)_6)_6 + 9Na_2SO_4 + Fe'''_2(SO_4)_3.$$

By treatment with an excess of a ferric salt solution; the whole of the basic ferrous iron, in the insoluble compound, is replaced by ferric iron, with formation of a blue compound similar in composition to the compounds obtained by precipitating the corresponding ferrocyanide with a ferric salt :

$$3Fe''_2Fe''(CN)_6 + 4Fe'''Cl_3 = Fe'''_4[Fe''(CN)_6]_3 + 6Fe''Cl_2.$$

When a ferrocyanide solution is distilled with a dilute mineral acid a ferrous ferrocyanide is produced :

$$2K_4Fe(CN)_6 + 3H_2SO_4 = 6HCN + Fe''K_2Fe(CN)_6 + 3K_2SO_4.$$

The compounds produced by this method have the

same composition as those prepared by double decomposition, and are practically identical, though they differ somewhat in certain reactions. They are generally more dense, and probably contain less combined water.

Ferrous ferrocyanide, $Fe''_2Fe(CN)_6$, is obtained in a state of purity by precipitating hydroferrocyanic acid or calcium ferrocyanide with ferrous chloride. By boiling with the alkaline carbonates or alkali metal salts it is converted into the double alkali metal ferrous ferrocyanide :

$$K_2CO_3 + Fe_2Fe(CN)_6 = FeK_2Fe(CN)_6 + FeCO_3.$$

It is readily decomposed by solutions of the caustic alkalis and also the alkaline earth metal hydroxides.

Ferrous ferrocyanide is also formed in a more dense form when calcium ferrocyanide solution is distilled with a dilute mineral acid :

$$3Ca_2Fe(CN)_6 + 12HCl = 12HCN + 6CaCl_2 + Fe''_2Fe(CN)_6.$$

The same compound is also obtained in the distillation of solutions of hydroferrocyanic acid, or when strontium or lithium ferrocyanides are distilled with a dilute acid.

When a ferrous salt is added to a solution of ammonium ferrocyanide in the presence of an excess of ammonium salts until the whole of the ferrocyanide is just precipitated, a white precipitate is obtained closely resembling the above, but differing in composition, half only of the base being ferrous iron, the other half consisting of ammonium, $Fe''(NH_4)_2Fe(CN)_6$. And a body of the same composition is obtained by distilling ammonium ferrocyanide solution with an acid. If, however, an excess of the ferrous salt is added to the ferrocyanide solution and in the absence of other ammonium salts, a white precipitate is formed approximating to the composition :

$$Fe''_4(NH_4)_4[Fe(CN)_6]_3 = Fe''_2Fe(CN)_6 : 2Fe(NH_4)_2Fe(CN)_6.$$

Ferrous magnesium ferrocyanide, $Fe''MgFe(CN)_6$, is

obtained by distilling magnesium ferrocyanide solution with a dilute acid or by precipitating the ferrocyanide solution with a ferrous salt solution, preferably in the presence of magnesium salts. The compound has the general properties of the ferrous ferrocyanides.

As in the case of the ammonium salts there are two ferrous potassium ferrocyanides, which differ from one another in the proportion of combined potassium.[1] The compound, $Fe''K_2Fe(CN)_6$, is produced by precipitating the potassium ferrocyanide solution exactly with the ferrous salt, avoiding excess, and preferably in the presence of other potassium salts, such as the chloride. It is also obtained when the ferrocyanide solution is distilled with an acid. If a large excess of the ferrous salt is used in the precipitation of the ferrocyanide solution and in the absence of other potassium salts, a precipitate is obtained containing only two-thirds of the combined potassium of the above compound, approximating in composition to the formula :

$$Fe''_4K_4[Fe(CN)_6]_3 = Fe''_2Fe(CN)_6 : 2Fe''K_2Fe(CN)_6.$$

The compound, $Fe''_4Na_4[Fe(CN)_6]_3$, is produced when a pure dilute solution of sodium ferrocyanide is precipitated with a ferrous salt. If the precipitation takes place in the presence of a large excess of sodium salts the composition of the precipitate approaches $Fe''Na_2Fe(CN)_6$. A compound of this composition is, however, readily obtained by distilling sodium ferrocyanide with a dilute mineral acid.

Several ferrocyanides containing both ferrous and ferric iron together combined in the base are known.[2]

When a solution of ammonium ferrocyanide is evaporated in the open air decomposition takes place with evolution of ammonium cyanide, and the formation of a very finely divided green compound. This compound is better prepared in a state of greater purity by gradually adding dilute ammonium chloride

[1] E. Mueller and W. Treadwell, *J. pr Chem.*, **80**, 170–82.

[2] H. E. Williams, *P.C.S.*, **29**, 411, 54.

drop by drop to a solution of sodium ferrocyanide boiling in an open dish. The green precipitate which settles fairly readily is somewhat difficult to filter, but when washed and air-dried, it has a composition agreeing with the formula :

$$Fe'''_2Fe''(NH_4)_8[Fe''(CN)_6]_4 3H_2O.$$

This body may be considered to consist of a compound of the double salts of ferrous and ferric ammonium ferrocyanide thus :

$$Fe'''_2Fe''(NH_4)_8[Fe''(CN)_6]_4 = Fe'''_2(NH_4)_6[Fe(CN)_6]_3 + Fe''(NH_4)_2Fe(CN)_6.$$

The corresponding ferrosoferric potassium ferrocyanide :

$$Fe'''_2Fe''K_8[Fe(CN)_6]_4 6H_2O$$

is prepared by gradually adding dilute hydrochloric acid solution drop by drop to a solution of potassium ferrocyanide, boiling in an open dish.

If dilute ammonium chloride solution is used in place of the dilute hydrochloric acid in the above method of preparation, a ferrosoferric ammonium potassium ferrocyanide is obtained in which seven-eighths of the potassium is replaced by ammonium :

$$Fe'''_2Fe''(NH_4)_7K[Fe''(CN)_6]_4 3H_2O.$$

These three compounds are very similar in appearance, and when washed and air-dried consist of fine powders of a dull slaty-green colour. They offer considerable resistance to the action of the alkalis, being practically unattacked by the carbonates of sodium and potassium even on boiling, but are slowly decomposed by caustic alkalis.

Ferrosoferric compounds of a dull blue colour may also be prepared. These compounds are similar in constitution to those above described, but contain one extra atom of ferrous iron in the molecule in place of two atoms of the alkali metal or ammonium. They may be denoted by the general formula :

$$Fe'''_2Fe''_2M'_6[Fe''(CN)_6]_4 XH_2O,$$

which may be considered as a molecular compound of one molecule of the ferric double salt combined with one molecule of ferrous ferrocyanide :

$$Fe'''_2Fe''_3M'_6[Fe''(CN)_6]_4 = Fe'''_2M'_6[Fe''(CN)_6]_3 + Fe''_2Fe''(CN)_6.$$

The sodium compound, $Fe'''_2Fe''_2Na_6[Fe(CN)_6]_4 \cdot 10H_2O$, is produced by adding dilute hydrochloric drop by drop to a solution of sodium ferrocyanide, boiling in an open dish in air contact. No green compound is formed as is the case with potassium or ammonium ferrocyanides, but a dull blue precipitate of the above composition.

The corresponding ammonium salt, $Fe'''_2Fe'''_2(NH_4)_6[Fe''(CN)_6]_4 2H_2O$, is prepared by first distilling ammonium ferrocyanide solution with an excess of dilute sulphuric acid, and after boiling the precipitated ferrous ammonium ferrocyanide for about half an hour it is oxidized while still hot with an excess of nitric acid. A mild oxidizing action takes place and the insoluble ferrocyanide is converted into a granular precipitate of a dull blue colour, which may be filtered and washed with ease.

These blue compounds are only partially decomposed by the carbonates of the alkalis, the ferrous ferrocyanide being unattacked :

$$Fe''_2Fe''_2Na_6[Fe(CN)_6]_4 + 4Na_2CO_3 + 3H_2O = 3Na_4Fe(CN)_6 + Fe''Na_2Fe(CN)_6 + Fe'''_2(OH)_6 + Fe''CO_3 + 3CO_2.$$

They are, however, completely decomposed by solutions of the caustic alkalis with precipitation of ferrosoferric hydroxide.

LEAD FERROCYANIDE, $Pb_2Fe(CN)_6 5H_2O$, is only prepared in the pure state by precipitating the hydrogen or the calcium salt with lead acetate solution. It is a heavy white powder insoluble in water, slightly soluble in alcohol, and easily soluble in ammonium chloride solution ; it is also soluble in hydrochloric acid and in nitric acid. By the latter acid it is converted into ferricyanide, and if the freshly precipitated lead compound be added to dilute nitric acid until it ceases to

be dissolved and the mixture then gently warmed, on neutralizing the solution with lead carbonate some nitroferricyanides will be found in solution.

LITHIUM FERROCYANIDE, $Li_4Fe(CN)_6 7H_2O$, may be readily obtained by decomposing the barium ferrocyanide with the equivalent quantity of lithium sulphate; on evaporating the filtrate a syrupy liquid is obtained, which crystallizes after some days.

The crystals are very soluble in water, and very deliquescent, and contain 7 molecules of water of crystallization and not nine as usually stated. When heated to 100° C., 4 molecules of water are driven off.

The double salts, $Li_2K_2Fe(CN)_6 3H_2O$ and $Li_2(NH_4)_2Fe(CN)_6 3H_2O$, are also said to be formed in crystallizing the two solutions together. They may be prepared by decomposing the barium potassium and the barium ammonium ferrocyanide respectively with the calculated quantity of lithium sulphate.

The solution of lithium ferrocyanide decomposes slightly when evaporated under normal pressure, and deposits a small quantity of ferric oxide.

MAGNESIUM FERROCYANIDE, $Mg_2Fe(CN)_6 12H_2O$, may be prepared from the barium salt in a similar manner to the preceding.

The salt separates from the evaporated solution in crystalline crusts of a pale yellow colour; slight decomposition occurs when the solution is evaporated under atmospheric pressure, and the crystals effloresce on exposure to the air.

The addition of potassium chloride or ferrocyanide solution to a moderately strong solution of magnesium ferrocyanide, or of a mixture of magnesium and potassium chlorides to sodium ferrocyanide solution, yields a white precipitate after a few seconds in the cold, and immediately on boiling, of a sparingly soluble double magnesium potassium ferrocyanide, $MgK_2Fe(CN)_6H_2O$. By substituting ammonium ferrocyanide or ammonium chloride for the potassium salts in the above method, a sparingly soluble double magnesium ammonium salt is obtained. This salt

may also be obtained by digesting the potassium double salt in an excess of ammonium chloride solution, when the potassium is completely replaced by ammonium. These double salts are sparingly soluble in water, the ammonium compound being less soluble than the potassium salt, and may be obtained with varying quantities of combined water, depending on the temperature at which the salt is precipitated and the concentration of the salts in the liquor. Thus Briggs [1] found 7 molecules of water in the salt prepared by boiling a 6 per cent. solution of potassium ferrocyanide with a 3 per cent. solution of magnesium chloride; while Robinson [2] obtained an anhydrous potassium compound by mixing the cold concentrated solutions of the two salts.

If a 5 per cent. solution of sodium ferrocyanide is precipitated at 100° C., with a large excess of a solution of magnesium and potassium chloride and magnesium and ammonium chloride respectively, precipitates are obtained which in each case contain but one molecule of water, thus: $MgK_2Fe(CN)_6H_2O$ and $Mg(NH_4)_2Fe(CN)_6$-H_2O.[3]

If the ammonium double salt is digested in an excess of potassium chloride solution in the cold, no action takes place, but if the mixture is boiled, part of the ammonium is replaced by potassium, with formation of the triple salt, $Mg_2K(NH_4)_3[Fe(CN)_6]_22H_2O$.[4]

When a strong solution of sodium ferrocyanide to which magnesium chloride has been added is boiled, a white sparingly soluble precipitate closely resembling those just described is formed of a double magnesium sodium ferrocyanide, $MgNa_2Fe(CN)_63H_2O$. This double salt is converted completely into the ammonium compound by digesting with a solution of an ammonium salt. A sparingly soluble double calcium salt may also be prepared, by boiling a strong solution of calcium ferrocyanide in which crystals of magnesium chloride are dissolved; the double salt separates out in white

[1] *T.C.S.* (1911), 1028.
[2] *T.C.S.* (1909), **95**, 1353.
[3] H. E. W.
[4] H. .E. W.

microscopic crystals of the composition $Mg_4Ca_2[Fe(CN)_6]_3 24H_2O$, which loses one-third of its combined water at 100° C.[1]

MANGANESE FERROCYANIDE, $Mn_2Fe(CN)_6 8H_2O$, may be prepared as a yellowish crystalline powder by the addition of calcium ferrocyanide solution to an excess of an acidified solution of manganese chloride. The precipitate which is at first obtained is white and bulky, but becomes crystalline on standing or stirring for a few minutes.

The compound is not decomposed by the boiling solutions of the alkaline carbonates, but is readily decomposed by the caustic alkalis.

This compound may also be prepared free from other base by precipitating the hydrogen, lithium or strontium ferrocyanides with an excess of a manganous salt. When precipitated from the alkali metal ferrocyanides dense white bulky precipitates are obtained containing alkali metal in combination: thus the compound, $Mn_6(NH_4)_8[Fe(CN)_6]_5$, is obtained when ammonium ferrocyanide solution is exactly precipitated with a manganese salt. With potassium ferrocyanide the compound, $Mn_6K_8[Fe(CN)_6]_5 9H_2O$, is obtained, which retains 6 molecules of water at 100° C. A dilute solution of sodium ferrocyanide free from other sodium salts when precipitated by manganese chloride solution yields a precipitate of the composition $Mn_7Na_2[Fe(CN)_6]_4 35H_2O$, which loses 15 molecules of water at 100° C. If, however, the precipitation takes place in the presence of a large excess of sodium chloride, the precipitate contains considerably more combined sodium and has the composition represented by the formula $Mn_7Na_6[Fe(CN)_6]_5$. Magnesium ferrocyanide, when precipitated with manganese chloride in the presence of an excess of magnesium chloride, yields the compound $Mn_8Mg_2[Fe(CN)_6]_5$.

All these manganese ferrocyanides are converted by strong hydrochloric acid into hydroferrocyanic

[1] H. E. W.

acid, and by dilute (1 to 3) acid into the acid salt, $MnH_2Fe(CN)_6 4H_2O$; when treated with nitric acid they are converted into the brown manganous ferricyanide, $Mn_3[Fe'''(CN)_6]_2 14H_2O$.

MERCURIC FERROCYANIDE. When mercuric chloride is added to a ferrocyanide solution a white precipitate is first formed, which, however, gradually decomposes on keeping, and turns blue; if an excess of the mercury salt is added and the mixture boiled, the ferrocyanide is decomposed with formation of mercuric cyanide.

MOLYBDENUM FERROCYANIDE .A dark red-brown precipitate may be obtained by the addition of an acidified solution of molybdic acid or a molybdate to a ferrocyanide solution.

NICKEL FERROCYANIDE, $Ni_2Fe(CN)_6 18H_2O$, is only obtained pure by precipitating the calcium or hydrogen ferrocyanide. It is precipitated as an apple-green voluminous precipitate, which when dried yields an olive-green powder. A number of different compounds may be obtained combined with an alkali metal.

The addition of a nickel salt to a solution of ammonium ferrocyanide, the latter being in slight excess, produces a bluish-green precipitate very difficult to filter of the double salt, $Ni(NH_4)_2Fe(CN)_6$. A similar potassium compound, $NiK_2Fe(CN)_6$, may be produced from potassium ferrocyanide in the presence of an excess of potassium chloride.

The compound, $Ni_5Ca[Fe(CN)_6]_3 21H_2O$, is prepared when calcium ferrocyanide is precipitated with a nickel salt, the former being in large excess; the compound loses six equivalents of water at 100° C. The strontium compound may be prepared in a similar manner, $Ni_5Sr(Fe(CN)_6)_3$. The exact precipitation of lithium ferrocyanide solutions forms the compound $Ni_7Li_2[Fe(CN)_6]_4$, and of magnesium ferrocyanide the compound, $Ni_7Mg[Fe(CN)_6]_4$, is obtained. By the addition of a large excess of the nickel salt solution to potassium ferrocyanide solution the compound,

$Ni_4K_4[Fe(CN)_6]_3 15H_2O = Ni_2Fe(CN)_6 : 2NiK_2Fe(CN)_6$, is obtained, which retains 12 molecules of water at 100° C. If the ferrocyanide solution is exactly precipitated with the nickel salt, the compound obtained has the composition $Ni_6K_8[Fe(CN)_6]_5$, and the sodium compound, $Ni_4Na_4[Fe(CN)_6]_3$, by exactly precipitating a solution of sodium ferrocyanide. If the precipitation takes place in the presence of an excess of sodium chloride, the compound has the composition $Ni_6Na_8[Fe(CN)_6]_5$.

All the above precipitates are of a more or less apple-green colour and are converted by strong hydrochloric acid into the nickel hydrogen salt, $NiH_2Fe(CN)_6 3H_2O$, and by boiling with the concentrated acid, finally into hydroferrocyanic acid.

Heated with strong nitric acid in the dry state particularly those containing a large proportion of combined alkali metal, a violent reaction takes place, and a dark brown powder is left, which when subsequently decomposed by caustic potash solution yields a brown insoluble matter of the hydroxides of nickel and iron, and a reddish solution which deposits bright red ferric hydroxide on boiling, the solution then containing ferrocyanides.

The nickel ferrocyanides are all soluble in ammonia solution, and by the addition of a ferrocyanide to a solution of nickel hydroxide in ammonia, beautiful lilac crystals separate out after a few seconds of a double compound of nickel ammonium ferrocyanide and ammonia, which can be obtained in the dry state only by drying the compound in an atmosphere of ammonia. When exposed to the air, or washed with water, ammonia is removed and the colour changes to green.

The following ammonia nickel compounds have been prepared :

$Ni_2Fe(CN)_6 4NH_3 H_2O$; $Ni_2Fe(CN)_6 2NH_3 4H_2O$; $Ni_2Fe(CN)_6 10NH_3 4H_2O$; $Ni_2Fe(CN)_6 8NH_3 4H_2O$; $Ni_2Fe(CN)_6 12NH_3 9H_2O$.

POTASSIUM FERROCYANIDE, $K_4Fe(CN)_6 3H_2O$, is an important commercial salt, and its manufacture has been described in detail in the section dealing with the manufacture of cyanogen compounds. It crystallizes in lemon-yellow or light amber-coloured tetragonal pyramids of a specific gravity of 1.86.

The crystals effloresce at 60° C., and become completely anhydrous at 100° C. This compound forms a number of soluble, sparingly soluble, and insoluble double and complex ferrocyanides with the ferrocyanides of other bases.

Iodine dissolved in the strong solution in sufficient quantities to produce a green colour forms the salt, $K_3Fe(CN)_6KI$, which crystallizes out. The solution also dissolves mercuric iodide, and on cooling deposits the double salt.

PYRIDINE FERROCYANIDE, $(C_5H_5N)_2H_2.H_2Fe(CN)_6 2H_2O$, is obtained as a sparingly soluble crystalline salt by adding pyridine chloride in an excess of hydrochloric acid to a solution of a ferrocyanide.

RUBIDIUM FERROCYANIDE, $Rb_4Fe(CN)_6 2H_2O$, is a very soluble salt which dissolves in less than its own weight of water.

The salt, $Rb_4Fe(CN)_6 3Hg(CN)_2 4H_2O$, has been prepared by D. Stromholm.[1]

SILVER FERROCYANIDE, $Ag_4Fe(CN)_6$, is precipitated in white curdy flocks by the addition of silver nitrate to a ferrocyanide solution. It is decomposed by alkali metal chlorides with liberation of the corresponding ferrocyanide, and it is soluble in ammonia, the solution of which when evaporated spontaneously without heating deposits the compound $Ag_4Fe(CN)_6 2NH_3 6H_2O$ (Gintl), but on heating silver ferrocyanide and ferric oxide are deposited and a double silver cyanide left in solution.

SODIUM FERROCYANIDE, $Na_4Fe(CN)_6 10H_2O$, is now of great commercial importance, and its manufacture is described in detail in the section dealing with the manufacture of commercial cyanogen compounds.

[1] *Z. anorg. Chem.* (1913), **84**, 208, 216.

It crystallizes easily from its solution in water in large well-formed lemon-yellow crystals, which effloresce in warm dry air, and lose the whole of the water of crystallization at 100° C. It is similar in properties to the potassium salt, and gives all the general reactions of the soluble ferrocyanides. The precipitates formed with the heavy metal salts always contain sodium in combination, though the amount is generally less than in the case of precipitates formed under identical conditions with potassium or ammonium ferrocyanide. It has but little tendency to form sparingly soluble double salts, the magnesium salt being the only known example. It forms soluble double salts with potassium ferrocyanide, and the compound, $Na_3NH_4Fe(CN)_6$, with ammonium ferrocyanide. The salt is less soluble in a solution containing other salts, and it is practically insoluble in the cold in a solution of 10 to 15 per cent. of sodium thiocyanate especially if 2 to 3 per cent. of sodium carbonate is also present.

STRONTIUM FERROCYANIDE, $Sr_2Fe(CN)_6 15H_2O$, is most conveniently prepared by boiling magnesium ammonium ferrocyanide with strontium hydroxide—this double salt being easily prepared by adding equivalent quantities of ammonium and magnesium chlorides to a solution of sodium ferrocyanide and washing the precipitate. When the whole of the ammonia is boiled off the solution is filtered, the excess of the strontium hydroxide removed by a current of carbon dioxide and the filtrate concentrated and crystallized. The salt is very soluble in water, a cold saturated solution at 15.5° C. has a specific gravity of 1.282, and 100 c.c. of the solution contain 31 grm. of $Sr_2Fe(CN)_6$ or 50.35 grm. $Sr_2Fe(CN)_6 15H_2O$. By allowing the solution to crystallize slowly, large crystals may be obtained.

When distilled in solution with dilute sulphuric acid it yields two-thirds of its cyanogen as hydrocyanic acid, the remainder being precipitated as ferrous ferrocyanide.

When a strong solution of the ferrocyanide is boiled

with ammonium chloride the double salt, $Sr(NH_4)_2Fe(CN)_6$, is precipitated as an anhydrous light yellow crystalline powder The corresponding potassium salt is obtained in a similar manner, $SrK_2Fe(CN)_6 3H_2O$. The sodium salt does not seem to exist.

TIN FERROCYANIDES. A solution of stannous chloride produces a white precipitate when added to a ferrocyanide solution. When stannic chloride is added to a solution of calcium ferrocyanide a white precipitate is formed which, when washed, dries up to an almost black vitreous mass. It has a composition agreeing with the formula $Sn^{iv}Fe(CN)_6 14H_2O$, and loses three molecules of water at 100° C. without decomposition.

THALLIUM FERROCYANIDE, $Tl_4Fe(CN)_6 2H_2O$, may be obtained in small glistening needles by double decomposition.

URANIUM FERROCYANIDE, $(UrO_2)_2Fe(CN)_6 5H_2O$, is a very dark brown compound insoluble in water, and is obtained by precipitating a solution of the calcium salt with uranium nitrate or acetate.

VANADIUM FERROCYANIDE, $(VO)_2Fe(CN)_6 11H_2O$, was obtained by Allenbury,[1] by precipitating potassium ferrocyanide with a solution of a vanadium salt. It, however, probably contains potassium.

YTTRIUM FERROCYANIDE, $Y_2Fe(CN)_6$, said to be obtained in non-efflorescent crystals by boiling ferric ferrocyanide with yttria. It is very soluble in water, and is said to form soluble double salts.

ZINC FERROCYANIDE, $Zn_2Fe(CN)_6 6H_2O$, like other heavy metal ferrocyanides, is only obtained pure from the calcium or hydrogen salt by precipitation with excess of zinc chloride. The precipitate, when washed and dried, is a white insoluble powder, insoluble in dilute hydrochloric acid, but when boiled with the strong acid, the whole of the zinc is abstracted, leaving a precipitate of hydroferrocyanic acid. When boiled with carbonate of sodium or potassium it is converted into a basic salt, part of the ferrocyanide passing into

[1] *Bl.* [2], **24**, 355.

solution. It is, however, completely soluble in a solution of potassium or sodium hydroxide, but it is converted into a white ammoniacal compound by ammonia solution which is completely insoluble in water and in excess of ammonia solutions.

Zinc ferrocyanide boiled with ferric chloride solution is completely converted into ferric ferrocyanides and when warmed with dilute nitric acid it is oxidized and converted into the orange-yellow zinc ferricyanide.

With the alkali metal or alkaline earth metal ferrocyanides, precipitates are obtained containing these metals in combination. By precipitating with zinc chloride solutions and using a large excess of the ferrocyanide double salts of the type $Zn_3M'_2(Fe(CN)_6)_2$ are obtained, but compounds of the type $ZnM_2Fe(CN)_6$ do not appear to exist, or if they exist are unstable.

The following compounds have been prepared by the method described above :[1]

$Zn_3Ca[Fe(CN)_6]_2XH_2O$; $Zn_3Li_2[Fe(CN)_6]_2XH_2O$;
$Zn_3Mg[Fe(CN)_6]_2XH_2O$; $Zn_3K_2[Fe(CN)_6]_228H_2O$;
$Zn_3Na_2[Fe(CN)_6]_24H_2O$; $Zn_3Sr[Fe(CN)_6]_29H_2O$.

The last compound loses three molecules of water when heated to 100° C.

[1] H. E. W.

CHAPTER V

IRON CYANOGEN COMPOUNDS

FERRICYANIDES, CARBONYLFERROCYANIDES, NITROFERRICYANIDES, PERFERRICYANIDES, ETC.

THE FERRICYANIDES. These compounds are produced from the ferrocyanides by oxidation, the ferrous iron being converted into ferric iron with the removal of one atom of the alkali metal of the base, giving rise to a series of compounds of the type $M'_3Fe(CN)_6$ or $M''_3[Fe(CN)_6]_2$, which may be regarded as complex double cyanides of ferric cyanide.

The potassium salt may be readily prepared by the method originally proposed by Leopold Gmelin, the discoverer of these compounds, which consists in passing chlorine through a moderately strong solution of the potassium ferrocyanide, keeping the liquid cool throughout the operation, until the solution produces no blue coloration when tested with a dilute ferric chloride solution :

$$2K_4Fe''(CN)_6 + Cl_2 = 2KCl + 2K_3Fe''(CN)_6.$$

The chlorine should not be passed through the liquor in excess, nor should the solution be allowed to become hot, or complex insoluble green iron cyanogen compounds will be produced, most difficult to remove.

When the reaction is complete the solution is evaporated on the water-bath and allowed to crystallize. The first crop of crystals obtained will be fairly pure, and may be rendered quite pure by recrystalliza-

tion, but the second crop will be contaminated with potassium chloride.

The salt is sometimes manufactured commercially by passing chlorine into a chamber containing layers of powdered and dry potassium ferrocyanide, in a manner somewhat similar to the manufacture of chloride of lime, but the salt is, of course, contaminated with potassium chloride.

It can be more readily prepared in the laboratory by substituting bromine for the chlorine, which has the advantage that as the bromine can be accurately weighed, it can be added to the ferrocyanide in the calculated amount.

Other oxidizing agents will also effect this conversion, and a variety of methods have been proposed for the formation of ferricyanides, the chief of which are outlined below.

1. Oxidation by calcium plumbate.[1] The calcium plumbate is added to the ferrocyanide solution in the proportion indicated by the equation given below, and a rapid stream of carbon dioxide passed through :

$$2K_4Fe(CN)_6 + PbO_2(CaO)_2 + 4CO_2 = 2K_3Fe(CN)_6 + K_2CO_3 + PbCO_3 + 2CaCO_3.$$

The carbon dioxide is necessary to allow the reaction to go to completion by carbonating the caustic alkalis which are first formed in the reaction. The calcium plumbate is prepared by roasting lime and lead oxide at a low heat, and may be reformed for use again by filtering off the precipitated lead and calcium carbonates, and roasting them after washing and drying.

By the addition of calcium ferricyanide prepared in a similar manner, to the solution of the ferricyanide prepared as above, the potassium carbonate may be removed and a pure solution of potassium ferricyanide obtained. It is advisable to add the calcium solution after the conversion of the potassium salt, as the potassium carbonate formed acts as a carrier of the carbon dioxide.[2]

[1] Kassner, *Chem. Zeit*, xiii. 1701 ; *J.C.S.I.*, ix. 391.

[2] *Chem. Zeit.* (1893), **17**, 1712 ; *J.S.C.I.*, **13**, 392.

2. When a stream of carbon dioxide is passed through a solution of a ferrocyanide containing lead peroxide in suspension, ferricyanide is formed by oxidation of the ferrocyanide.[1]

3. Seuberlich's method.[2] The calculated quantity of hydrochloric acid is added to the solution of potassium ferrocyanide and shaken with an excess of lead peroxide in the cold.

4. In 200 c.c. of distilled water 26 grm. of potassium ferrocyanide are dissolved and 8 c.c. of strong hydrochloric acid added, followed by 2 grm. of potassium permanganate dissolved in 300 c.c. of water, the latter being slowly added.

The excess of acid is neutralized by calcium or barium carbonate, and the filtrate evaporated on the water-bath. Only the first crop of crystals obtained, however, will be pure.[3]

The use of chlorine as an oxidizing agent is quite satisfactory for the preparation of the potassium salt, but is not applicable for the preparation of the sodium, ammonium, or the alkaline earth metal salts, chiefly on account of the greater solubility of the ferricyanides of these bases and the great difficulty, and in many cases the impossibility, of separating them in a pure condition from the associated chloride. Of the other methods described above they are either tedious or give rise to other salts from which it is difficult to separate the ferricyanide.

This difficulty may be overcome by the process described below, whereby good yields may be obtained of the ferricyanides of the alkali or alkaline earth metals entirely free from any other salts or discoloration due to the formation of traces of blue or green iron cyanogen compounds.[4]

To 100 grm. of sodium ferrocyanide dissolved in 1000 c.c. of water add a solution of manganese chloride

[1] Schronbein's Method, abst. *J.C.S.* (1881), p. 323.
[2] *J.C.S.* (1881), p. 239.
[3] *J. Am. Chem. Soc.*, 17 (1895), 68 ; *J.S.C.I.*, 14, 691.
[4] H. E. Williams.

or sulphate until the ferrocyanide is completely precipitated. The mixture, which contains white manganous ferrocyanide of the formula $Mn_7Na_2[Fe(CN)_6]_4$ in suspension, is raised to the boil, and nitric acid added until oxidation is complete. By this means the white manganous ferrocyanide is converted into the brown manganous ferricyanide, $Mn_3[Fe'''(CN)_6]_2$. The mixture is then thrown on a vacuum filter and thoroughly washed; this is not a lengthy operation as the brown precipitate filters fairly well. The washed paste is then added to a solution of a ferrocyanide and agitated when the following reaction takes place, thus with sodium ferrocyanide:

$$7Mn_3[Fe'''(CN)_6]_2 + 12Na_4Fe''(CN)_6 = 14Na_3Fe'''(CN)_6 + 3Mn_7Na_2[Fe''(CN)_6]_4.$$

And with calcium ferrocyanide:

$$2Mn_3[Fe'''(CN)_6]_2 + 3Ca_2Fe''(CN)_6 = 2Ca_3[Fe'''(CN)_6]_2 + 3Mn_2Fe''(CN)_6.$$

The addition of the brown manganous ferricyanide must be continued until it ceases to turn white on agitation, and some of the brown compound remains in excess. The liquid is then filtered off and the pure ferricyanide solution evaporated under reduced pressure; the washed precipitate of white manganous ferrocyanides may be made into a thin cream with water and reoxidized with nitric acid and used for the conversion of a fresh quantity of ferrocyanide.

The formation of ferricyanides by the above described process takes place in the cold for all soluble salts except the ammonium salt. In this case the conversion only takes place on heating. This salt is, however, best prepared by precipitating a solution of the barium salt with sulphate of ammonium solution.

A process on the same lines as the above was proposed by Williamson,[1] who endeavoured to make use of the blue compound produced by the oxidation of the double ferrous ferrocyanide by nitric acid. This

[1] *A.* (1846), **57**, 225.

blue when filtered and washed and digested in a solution of a ferrocyanide is converted into the white ferrous ferrocyanide, while the soluble ferrocyanide is oxidized to a ferricyanide, but the process is almost impossible to carry out principally owing to the difficulty of filtering the very bulky and slimy precipitate, a difficulty which is absent from the process above described with the manganese ferricyanide.

The ferricyanides of the alkali and alkaline earth metals, including those of lithium, magnesium, and lead, are soluble in water, from which they may be made to crystallize in fine ruby red or brownish-red crystals. No sparingly soluble double salts of the alkali metal with the alkaline earth metal ferricyanides appear to exist.

As in the case of the ferrocyanides, neither the iron nor the cyanogen group can be detected by the ordinary reagents, and they do not possess the violent poisonous properties of the simple soluble cyanides. The ferricyanogen group, $'''Fe(CN)_6$, forms a negative radicle which can be displaced by double decomposition with other acid radicles.

The ferricyanides are reduced to ferrocyanides by hydrogen sulphide, ferrous, stannous, manganous, cobaltous, or chromous hydroxides, and when warmed with caustic alkalis. A reducing action is also exerted by such compounds as sulphites, cyanides, oxalates, and phosphites: alcohol, sugar, starch, and cellulose, particularly when exposed to light or heat.

They are also reduced by reduced metallic iron, nickel, zinc and silver in an atmosphere of hydrogen.[1] Thus with metallic iron:

$$4K_3Fe'''(CN)_6 + 2Fe = 2Fe''K_2Fe''(CN)_6 + 2K_4Fe''(CN)_6.$$

When boiled with mercuric oxide, the ferricyanides are completely decomposed with formation of mercuric cyanide, and an alkaline hydroxide in solution and precipitation of ferric oxide:

$$2K_3Fe(CN)_6 + 6HgO + 3H_2O = 6Hg(CN)_2 + 6KOH + Fe_2O_3.$$

[1] G. Smith and R. A. Lynd, *Z. anorg. Chem.* (1913), **82**, 6270; *J.C.S.* i. 838 (1913).

When boiled with mercuric chloride, the solution becomes first of a deep permanganate colour and then deposits a green precipitate, but it is ultimately completely decomposed by further boiling into mercuric cyanide.

When heated with strong sulphuric acid, ferricyanides like the ferrocyanides are completely decomposed, giving rise to similar products.

Most of the ferricyanides of the heavy metals are insoluble in water, and in many cases exhibit characteristic colours usually differing markedly from the corresponding ferrocyanides, and they are obtained in the form of voluminous gelatinous precipitates. When prepared from the alkali metal ferricyanides these precipitates contain varying amounts of alkali metal in combination, but the amount so retained is usually much less than the corresponding ferrocyanides prepared under similar conditions.

No precipitation takes place in a cold solution of a ferricyanide by the addition of aluminium, cerium, chromium, lead mercury or thorium salts.

When a ferric salt solution is added to a moderately dilute solution of a ferricyanide, no precipitate occurs, the colour of the liquid merely becomes darker, thus affording a marked distinction from the ferrocyanides. Ferrous salts produce a deep blue precipitate, copper salts a yellowish-green, and silver salt an orange-red precipitate.

When digested on the water-bath with nitric acid (1 to 1), the soluble ferricyanides are converted into nitroferricyanides. This conversion can also be brought about by adding a nitrite and acidifying with acetic acid.

Most reducing agents reduce ferricyanides in solution to ferrocyanides :

$$2FeO + 2K_3Fe(CN)_6 + 2KOH = 2K_4Fe(CN)_6 + Fe_2O_3 + H_2O.$$

Cupric thiocyanate warmed with a solution of potassium ferricyanide reduces it with formation of an

insoluble precipitate of the red-brown cupric potassic ferrocyanide, and potassium thiocyanate in solution :

$$K_3Fe(CN)_6 + Cu'CNS = Cu''K_2Fe(CN)_6 + KCNS.$$

Several of the insoluble ferricyanides such as those of zinc, cadmium, etc., can be formed from the ferrocyanide salts by heating with strong nitric acid.

The addition of iodine to a solution of a ferricyanide produces on warming a dark coloured liquor, due to the formation of an iron cyanogen compound known as a perferricyanide

Ferricyanides in solution are reduced to ferrocyanides by potassium iodide in presence of an excess of hydrochloric acid and zinc sulphate, the latter being required to remove the ferrocyanide as it is formed and prevent a reverse action from setting in :

$$K_3Fe(CN)_6 + KI = K_4Fe(CN)_6 + I.$$

That the ferricyanides are capable of existing in two isomeric modifications has been shown by J. Locke and G. H. Edwards,[1] and are known as the α or red salts and the β or green salts. These two series differ but little in chemical properties. It is stated that the bismuth salt of the α compound is sparingly soluble and yellow, whereas the β compound is not precipitated ; the α potassium salt is anhydrous while the β salt crystallizes with one molecule of water, that stannic chloride produces no precipitate with the α salt but yields a precipitate with the β salt, and that the β lead salts are more soluble than the corresponding α salt.

According to Bellucci and G. Sabatini [2] the α compounds contain the six — (CN) groups, while the β compounds contain six — (NC) groups.

The existence of this isomerism is, however, denied by O. Hauser and E. Biesalski,[3] who allege that the β compound is simply the ordinary salt containing some

[1] *Am. Chem. J.*, **21**, 183, 413.
[2] *Atti R. Accad. Lincei*, **20**, i. 239–43.
[3] *Ber.* (1912), **45**, 3516–21.

prussian blue in colloidal solution, and that an artificial mixture of potassium ferricyanide and prussian blue give all the reactions of the β isomer. This, however, does not explain the statements with regard to the reactions of the two salts with bismuth, etc.

THE METALLIC FERRICYANIDES

AMMONIUM FERRICYANIDE, $(NH_4)_3Fe(CN)_6$, is described by Bette [1] as crystallizing in ruby-red needles stable in the air. By decomposing silver ferricyanide with the theoretical quantity of ammonium chloride, N. Tarugi [2] prepared it in tiny green crystals which become blue in the air although stable in solution out of air contact. When prepared by precipitating the barium salt solution with the exact amount of ammonium sulphate, the author obtained the salt in ruby red crystals which are anhydrous and quite stable in the air, and more stable when heated in solution than the corresponding ferrocyanide. When evaporated over calcium chloride or sulphuric acid, the solution is stable and crystallizes well in large, well-formed crystals. The solution may also be evaporated in vacuo with but slight decomposition. The double salt, $NH_4PbFe(CN)_6 3H_2O$, has been obtained by Schuller.[3]

BARIUM FERRICYANIDE, $Ba_3[Fe(CN)_6]_2 20H_2O$, is easily prepared by agitating barium ferrocyanide with a slight excess of manganous ferricyanide with sufficient water, and evaporating the filtered solution under a vacuum. It crystallizes very well in fine red crystals which are quite stable, and very soluble in water. In very dry air the crystals effloresce, and in this manner lose 8 molecules of water when exposed to calcium chloride, and a further 8 molecules when heated to 100° C. From this salt other soluble ferricyanides, the sulphates of which are soluble in water, may be conveniently prepared by double decomposition.

[1] *Annalen* (1837), **23**, 1.
[2] *Gazz.* (1896), **26**, ii. 25–28.
[3] *W.A.B.*, **77**, 692.

BISMUTH FERRICYANIDE is obtained by direct precipitation as a yellow insoluble precipitate. It may also be prepared by oxidizing the ferrocyanide with dilute nitric acid.[1] A solution of the so-called β potassium ferricyanide is said to give no precipitate with a bismuth salt.

CADMIUM FERRICYANIDE is an orange-yellow insoluble powder obtained by double decomposition. The pure compound is obtained only from the calcium or hydrogen salt solution. With the alkali metal ferricyanides precipitates are obtained containing small proportions of the alkali metal in combination; thus the compound obtained from potassium ferricyanide has a composition agreeing with the formula $Cd_{10}K[Fe'''(CN)_6]_7 72H_2O$, which loses thirty equivalents of water at 100° C. Cadmium ferricyanide is soluble in ammonia solution, from which it is separated combined with ammonia. It is also soluble in hydrochloric acid, and it is completely decomposed by solutions of the alkali metal carbonates.

CALCIUM FERRICYANIDE, $Ca_3[Fe'''(CN)_6]_2 15H_2O$, which may readily be prepared in a similar manner to the barium salt, crystallizes in small crystals very soluble in water; the crystals effloresce in dry air over calcium chloride or concentrated sulphuric acid, and at 100° C. lose 7 molecules of water. The compound is quite stable in the dry state in the air and at 100° C., and the aqueous solution is quite as stable as that of the potassium salt under normal conditions, but evolves some hydrocyanic acid when boiled, and deposits some ferric oxide. This decomposition may be expressed:

$$Ca_3[Fe'''(CN)_6]_2 + 9H_2O = 12HCN + Fe_2O_3 + 3Ca(OH)_2.$$

With pure neutral solutions no prussian blue is formed. When evaporated under considerably reduced pressure but little decomposition occurs.

A double salt, $CaKFe(CN)_6$, has been described by Mesander.[2]

[1] Pattison Muir, *C.J.*, **2**, 16, 654. [2] *P.*, **25**, 390.

CERIUM FERRICYANIDE, $CeFe(CN)_6 4H_2O$, has been prepared by Jalin [1] by the addition of alcohol to the mixed solutions of cerium nitrate and potassium ferricyanide.

CHROMIUM FERRICYANIDE. The composition of this salt has not yet been completely investigated, but Christensen has described the salt, $CrFe(CN)_6 5NH_3 \cdot 1\frac{1}{2}H_2O$.

COBALT FERRICYANIDE, $Co_3[Fe(CN)_6]_2 16H_2O$, is a red-brown insoluble powder obtained by precipitation from the calcium salt. It is insoluble in hydrochloric acid, but dissolves completely in ammonia. When treated with aqueous potassium or sodium hydroxide it is decomposed with formation of the insoluble black cobaltocobaltic hydroxide and a ferrocyanide of the alkali metal in solution :

$$Co_3[Fe(CN)_6]_2 + 8KOH = 2K_4Fe(CN)_6 + Co_3O_4 + 4H_2O.$$

The alkali metal ferricyanides yield precipitates of cobalt ferricyanide which contain some alkali metal in combination, thus the potassium salt precipitated by an excess of a cobalt salt solution yields a precipitate which does not differ in appearance or properties with the pure compound above described, but it contains some small quantity of potassium.

The compound, $Co_3[Fe(CN)_6]_2 2NH_3 6H_2O$, is described by Braun,[2] who obtained it by digesting the ferricyanide in cold liquid ammonia for some time.

CUPRIC FERRICYANIDE, $Cu_3[Fe(CN)_6]_2 14H_2O$, is a yellowish-green insoluble precipitate obtained from the calcium salt. It is insoluble in hydrochloric acid, but is soluble in ammonia solution. At 100° C. 8 molecules of water are driven off. This compound is also formed by passing chlorine through a suspension in water of recently precipitated cupric ferrocyanide. A brownish compound of cupric ferroferricyanide is produced by the action of boiling nitric acid on dry and ground cupric ferrocyanide, $Cu_5[Fe(CN)_6]_3 27H_2O = Cu_5[Fe''Fe'''_2(CN)_{18}] = Cu_2Fe''(CN)_6\,Cu_3[Fe'''(CN)_6]_2$.

[1] *Ber.* [2], **21**, 535 [2] *A.*, **125**, 153, 197.

The precipitates obtained from the alkali metal ferricyanides contain but a very small portion of alkali metal in combination. The compound prepared from the sodium salt contain 0.1 per cent. sodium and from the potassium salt 0.168 per cent. of potassium.

Freshly prepared cupric ferricyanide is immediately converted into the brown ferrocyanide when digested in a ferrocyanide solution :

$$Cu_3[Fe(CN)_6]_2 + 2K_4Fe(CN)_6 = 2K_3Fe(CN)_6 + Cu_3K_2[Fe(CN)_6]_2.$$

CUPROUS FERRICYANIDE. The addition of a solution of a cuprous salt to a solution of a ferricyanide produces a red-brown precipitate, and the same product is formed by digesting cuprous thiocyanate in the ferricyanide solution. This red precipitate is not, however, cuprous ferricyanide, but cupric potassic ferrocyanide :

$$K_3Fe'''(CN)_6 + Cu'Cl = Cu''K_2Fe''(CN)_6 + KCl.$$

HYDROFERRICYANIC ACID, $H_3Fe(CN)_6$, may be prepared in a similar manner to hydroferrocyanic acid, by decomposing the lead or barium salt with the theoretical quantity of sulphuric acid ; by the addition of hydrochloric acid to suspensions of silver ferricyanide ; or by adding hydrochloric acid to a solution of the potassium salt and precipitating the acid by the addition of ether.

It may be recovered from its solutions in red-brown needles by gentle evaporation under a vacuum. It is a strong acid and easily decomposes the carbonates of the alkali and alkaline earth metals, and it is very soluble in water and alcohol.

IRON FERRICYANIDES — FERRIC FERRICYANIDE. This compound has not yet been isolated, the addition of a ferric salt only produces a deep brown coloured liquid. If a solution of barium ferricyanide is exactly precipitated with ferric sulphate and filtered, a brown liquid is obtained, which must consist essentially of a solution of ferric ferricyanide, which, however, cannot be evaporated without rapid decomposition.

If a strong solution of ferric chloride is added to a very strong solution of a ferricyanide such as may be obtained by the use of the lithium or sodium salt, the mixture rapidly becomes warm and deposits a green precipitate with copious evolution of chlorine; on warming with the addition of more ferric chloride if necessary, the green compound is changed to blue with a further evolution of chlorine thus:

(1) $12Na_3Fe'''(CN)_6 + 14Fe'''Cl_3 = 2Fe_7[Fe'''Fe''(CN)_{12}]_3 +$
green ferric ferroferricyanide
$36NaCl + 3Cl_2.$

and:

(2) $2Fe'''_7[Fe'''Fe''(CN)_{12}]_3 + 2Fe'''Cl_3 = 4Fe_4[Fe(CN)_6]_3 + 3Cl_2.$

Although pure ferric ferricyanide is unknown in the solid state, green insoluble double salts of ferric ferricyanide and ferric ferrocyanide may be prepared.[1] If potassium ferrocyanide is precipitated in the presence of an excess of more than three times as much potassium ferricyanide, with ferric chloride, a very finely divided green precipitate is obtained, which when washed and dried has a composition agreeing with the formula:

$$Fe'''_{29}K_3[Fe''Fe'''_2(CN)_{18}]_9 2 10H_2O,$$

in which the ratio of ferro to ferricyanide is as 1 : 2. This compound can be considered as a double salt of ferric ferricyanide and ferric potassium ferrocyanide, thus: $18Fe'''Fe'''(CN)_6 : Fe'''_{11}K_3[Fe''(CN)_6]_9$. It is of interest to note that the ferric potassium ferrocyanide is identical with the compound obtained when potassium ferrocyanide is precipitated with ferric chloride in presence of excess of potassium salts. By eliminating the potassium, the formula of the compound would be, $Fe'''_{10}[Fe''Fe'''_2(CN)_{18}]_3 = Fe'''_4[Fe''(CN)_6]_3 : 6Fe'''Fe'''(CN)_6$, in agreement with the composition of the precipitate obtained when the calcium salts are substituted for the potassium compounds.

Pelouze's green obtained by passing chlorine through

[1] H. E. Williams, *P.C.S.* (1913), vol. xxix. p. 54.

a solution of a ferrocyanide, or a ferricyanide in excess,[1] may also be prepared by boiling ordinary dried and ground ferric ferrocyanide with strong nitric acid. The compound has the empirical formula, $Fe_{12}(CN)_{36}$, and was considered by Williamson to be a ferrosoferric ferricyanide, $Fe'''_4Fe''_3[Fe'''(CN)_6]_6$. It is more probable, however, that the compound is a ferric ferroferricyanide, thus: $Fe_7[Fe''Fe'''(CN)_{12}]_3 54H_2O = Fe'''_4Fe''(CN)_6 : 3Fe'''Fe'''(CN)_6$, the action of the nitric acid being merely to oxidize half the ferrocyanogen in the prussian blue to ferricyanogen.

If ferric potassium ferrocyanide is substituted for the ferric ferrocyanide, three-quarters of the ferrocyanogen may be oxidized, and the compound, $Fe'''_{13}[Fe''Fe'''_3(CN)_{24}]_3 100H_2O = Fe_4[Fe(CN)_6]_3 : 9Fe'''Fe'''(CN)_6$, obtained. This compound may also be produced by passing chlorine through freshly precipitated ferric ferrocyanide suspended in water. When washed and dried the compound is of a fine green colour, and loses water equivalent to 36 molecules when dried over calcium chloride.

These green compounds are decomposed when digested in a solution of a ferrocyanide with formation of a ferricyanide in solution, the green compound changing to prussian blue, and when boiled with ferric chloride solution chlorine is evolved with a similar transformation of green to blue :

(1) $Fe'''_7[Fe''Fe'''(CN)_{12}]_3 + 4K_4Fe''(CN)_6 = 3K_3Fe'''(CN)_6 + 7Fe'''KFe''(CN)_6$

and :

(2) $2Fe'''_7[Fe''Fe'''(CN)_{12}]_3 + 2FeCl_3 = 4Fe_4[Fe(CN)_6]_3 + 3Cl_2$.

The compound, $Fe'''_3K_2[Fe''_2Fe'''(CN)_{12}]6H_2O$, may be obtained by oxidizing with nitric acid in excess, the boiling aqueous suspension of ferrous potassium ferrocyanide prepared by distilling potassium ferrocyanide solution with dilute sulphuric acid. The compound is obtained as a violet, somewhat dense powder, which

[1] Pelouze, *Ann. Chim. Phys.* [2], **69**, 40 ; and Williamson, *A.*, **57**, 225.

when suspended in water appears dirty green by transmitted light, but a fine violet by reflected light. This compound may be considered as a double salt of 2 molecules of ferric potassium ferrocyanide combined with 1 molecule of ferric ferricyanide :

$$Fe'''_3K_2[Fe''_2Fe'''(CN)_{18}] = 2Fe'''KFe''(CN)_6 : Fe'''Fe'''(CN)_6.$$

FERROUS FERRICYANIDE. The addition of an excess of a ferrous salt to a solution of potassium ferricyanide results in the formation of a blue precipitate known as Turnbull's blue. This blue compound is, however, not a ferrous ferricyanide as has been shown by Hoffmann, Muller and others, but a potassium ferrosoferric ferrocyanide of the composition $Fe'''_3Fe''K[Fe(CN)_6]_3$: if the ferricyanide is incompletely precipitated by the ferrous salt, the former being in large excess, a blue precipitate is obtained of the composition $FeKFe(CN)_6$. This compound seems to be identical in composition and properties to soluble berlin or prussian blue obtained by adding a ferric salt to a large excess of potassium ferrocyanide solution : this identity was first pointed out by Scraub.[1] This point is; of course, very difficult of proof, but so far no differences in properties or composition has been detected between the two blues, the formation of which may be expressed thus :

(1) $K_4Fe''(CN)_6 + Fe'''Cl_3 = Fe'''KFe''(CN)_6 + 3KCl.$
(2) $K_3Fe'''(CN)_6 + Fe''Cl_2 = Fe'''KFe''(CN)_6 + 2KCl.$

It is probable that in the latter reaction the ferricyanide is first reduced by the ferrous chloride, and the reaction then proceeds as expressed in the first equation or that the two iron atoms are united to the cyanogen group in a similar manner.

The precipitate obtained from calcium ferricyanide solution and ferrous chloride has the composition $Fe''Fe'''_2[Fe''(CN)_6]_3$, or ferrosoferric ferrocyanide. This precipitate has the same composition whether the iron salt or the ferricyanide be in excess. When the blue

[1] *A.* **186**, 385 (1874).

is decomposed by a caustic alkali ferrocyanide is obtained in solution and a black ferrosoferric hydroxide thrown out :

$$Fe''Fe'''_2(Fe(CN)_6)_2 + 8KOH = 2K_4Fe(CN)_6 + Fe_3O_4 + 4H_2O.$$

If the white potassium ferrous ferrocyanide formed by precipitating potassium ferrocyanide solution with a ferrous salt not in excess be gently warmed with dilute nitric acid, oxidation takes place and a blue compound with a violet reflex is produced. This compound is probably a ferrous potassium ferricyanide, for when the compound, after thorough washing, is digested in a solution of potassium ferrocyanide, the blue compound is converted more or less into the white ferrous potassium ferrocyanide, and a ferricyanide is produced in solution. When the blue is decomposed by caustic alkalis only ferrocyanide is obtained in solution with precipitation of ferric hydroxide; the reason of this is of course that the ferrous hydroxide at first thrown out is immediately oxidized by the ferricyanide:

$$2Fe''KFe'''(CN)_6 + 6KOH = Fe_2O_3 + 2K_4Fe(CN)_6 + 3H_2O.$$

LITHIUM FERRICYANIDE, $Li_3Fe(CN)_6 7H_2O$, is prepared from the barium salt and lithium sulphate by double decomposition. It is a very soluble salt and crystallizes in reddish-brown needles which are deliquescent in moist air, but effloresce in dry air. When heated to 100° C. the crystals give off 5 molecules of water with slight decomposition. Some considerable decomposition takes place when the solution is boiled at the ordinary atmospheric pressure, but it may be concentrated under reduced pressure and the crystals obtained by evaporating the so concentrated liquor, over calcium chloride or strong sulphuric acid.

LEAD FERRICYANIDE is described by Gmelin as being anhydrous, by Schuller [1] as combined with 4 molecules of water, and by Zapharouch [2] as crystallizing with 16 molecules of water. Equivalent quan-

[1] *W.A.B.*, 77, 692. [2] *W.A.B.*, 59, 2nd pt., 800.

tities of lead nitrate and potassium ferricyanide in solution yield on cooling, according to Wyrubow,[1] crystals of the salt containing 16 molecules of water: he also describes a double salt with potassium:

$$PbKFe(CN)_6 3H_2O.$$

The double salt, $Pb_3[Fe(CN)_6]_2Pb(NO_3)_2 12H_2O$, has been described by Schuller (*l.c.*). This salt is also described by Enrich Müller and Otto Diefenthäler,[2] who gave the formula $Pb_2Fe(CN)_6NO_3 5H_2O$, and suggested the constitution, $NO_3 - Pb \cdot Pb : Fe(CN)_6$ or $Pb : Fe(CN)_6 PbNO_3$.

Lead ferricyanide is very soluble in water and crystallizes in small dark red crystals.

MAGNESIUM FERRICYANIDE, $Mg_3[Fe(CN)_6]_2 \cdot 18H_2O$, is an exceedingly soluble salt easily prepared from the sulphate and a solution of the barium salt. The solution decomposes when boiled under atmospheric pressure, but may be readily concentrated under reduced pressure. It crystallizes in red crystalline crusts that are quite stable.

The double salt, $MgKFe(CN)_6$, was obtained by Reindel.[3]

MANGANESE FERRICYANIDE, $Mn_3[Fe(CN)_6]_2 \cdot 14H_2O$, is obtained as a brown compound by precipitating calcium ferricyanide with manganous chloride, or by oxidizing manganous ferrocyanide with nitric acid. The air-dry compound when heated to 100° C. loses 2 molecules of water. When digested in a solution of a ferrocyanide the brown compound is immediately converted into the white manganous ferrocyanide, while the corresponding quantity of ferricyanide is formed in solution. This reaction affords a convenient means for the preparation of pure solutions of the soluble ferricyanides from the ferrocyanides. The salt, when decomposed by an alkali, is converted into

[1] *Ann. Chim. Phys.* [5], 10, 413.
[2] *Ber.* (1910), 43, 2321–23.
[3] *J. pr. Chem*, 103, 166.

manganomanganic hydroxide and a soluble ferrocyanide : this reaction may be expressed :

$$Mn_3[Fe'''(CN)_6]_2 + 8KOH = 2K_4Fe''(CN)_6 + Mn_3O_4 + 4H_2O.$$

MERCURIC FERRICYANIDE cannot be obtained by direct precipitation. When mercuric chloride solution is added to a soluble ferricyanide, no precipitate is formed, but on heating, the mixed solutions turn first a deep permanganate colour, which on further heating deposits a green precipitate, and the filtered solution, if sufficiently concentrated, will deposit crystals of a double salt on cooling. By continued boiling of the solution the ferricyanide is completely decomposed with formation of mercuric cyanide.

NICKEL FERRICYANIDE, $Ni_3[Fe(CN)_6]_2 18H_2O$, obtained by precipitation from the calcium salt, is an orange-brown precipitate, which when washed and dried forms dark, almost black, granules which are orange-yellow when ground. It is insoluble in hydrochloric acid, but completely soluble in ammonia solution, and when heated to 100° C. only 4 molecules of water are driven off. The addition of a ferricyanide solution to an ammoniacal solution of a nickel salt produces a yellow precipitate, said to have the composition $Ni_3[Fe(CN)_6]_2 4NH_3 4H_2O$.

POTASSIUM FERRICYANIDE, $K_3Fe(CN)_6$, was discovered by L. Gmelin in 1821, and was the first member of this series of compounds to be prepared. It may be obtained by passing chlorine through the ferrocyanide solution ; by the method described for the barium salt ; or it may be obtained from the solution of the latter by precipitating the barium with potassium sulphate. As the salt is much more soluble in hot water than cold, and crystallizes well, it may easily be obtained pure by the chlorine method.

The salt crystallizes in fine ruby-red triclinic crystals which are anhydrous. It is said that an isomeric β compound exists, which crystallizes with 1 molecule of water. The salt is very stable in the solid state, and

the solution keeps fairly well in the absence of organic reducing agents if shielded from the daylight. It is said to form a series of double salts with sodium ferricyanide, thus: $KNa_2Fe(CN)_6$; $K_2NaFe(CN)_6$; $K_3Na_3[Fe(CN)_6]_2$.[1] An unstable compound with potassium iodide, $K_3Fe(CN)_6KI$, has also been described.[2]

The solution of potassium ferricyanide is intensely yellow, and in presence of caustic alkalis is a powerful reducing agent.

SILVER FERRICYANIDE, $Ag_3Fe(CN)_6$, is precipitated as an orange-red clotty precipitate by the addition of silver nitrate to a soluble ferricyanide solution. The precipitate contains no alkali metal in combination, and when air-dried it is anhydrous. The compound is decomposed by hydrochloric acid and soluble chlorides, and it is soluble in ammonia solution. A solution of potassium ferricyanide added to an ammoniacal solution of silver nitrate, to which just sufficient ammonia has been added to form a clear solution, separates the compound, $2Ag_3Fe(CN)_63NH_3$-$\frac{1}{2}H_2O$.[3]

According to Carlo Gastaldi,[4] when a concentrated solution of potassium ferricyanide is added to ammoniacal silver nitrate, a deep red crystalline precipitate is deposited of the compound, $[Ag_3Fe(CN)_6]_25NH_3$. If the conditions are varied it is obtained as an amorphous flocculent precipitate, but it may be obtained in large crystals, by dissolving silver ferricyanide in ammonia solution and evaporating at the ordinary temperature, the composition of the compound being the same in whatever manner it is prepared. Compounds of similar composition may be prepared by replacing the ammonia by ethyl or methylamine.

If the ammoniacal solution is boiled, decomposition

[1] Reindel, *J. pr. Chem.*, **102**, 43; Laurent, *J.* (1849), 291; Wyrubow, *Bl.* [2], 1498, 14, 145.

[2] Preuss, *A.*, **29**, 323; Mohr, *A.*, **105**, 57; Blomstrand, *J. pr. Chem.* [2], **3**, 207.

[3] Gintl, *W.A.B.*, **59**, 559.

[4] *Gazz.* (1910), **46**, ii. 475–81; *J.C.S.* (1911), **1**, 185.

of the ferricyanogen takes place: the same action occurs when silver ferricyanide is boiled with caustic alkalis, silver oxide being first precipitated, but further action then rapidly takes place, ferric hydroxide being precipitated and a double silver cyanide left in solution.

SODIUM FERRICYANIDE, $Na_3Fe(CN)_6 2H_2O$, may be obtained in a state of great purity by the method used for the preparation of the barium and calcium salt. The solution decomposes when evaporated under ordinary pressure, but under reduced pressure it may be obtained with ease in red-brown crystals which are very soluble in water and deliquescent in moist air, and when heated to 100° C. lose water and become anhydrous. The properties of sodium ferricyanide are very similar to those of the potassium salt.

STRONTIUM FERRICYANIDE, $Sr_3[Fe(CN)_6]_2 12H_2O$, prepared in the same method as the barium salt, forms very soluble reddish-brown crystals, which effloresce in very dry air and lose 2 molecules of water, and a further 4 molecules are driven off at 100° C. The solution is not so stable as the salts of the alkali metals, and decomposes when evaporated under atmospheric pressure, but may be evaporated under reduced pressure.

ZINC FERRICYANIDE, $Zn_3[Fe(CN)_6]_2 13H_2O$, as obtained by precipitation of the calcium salt, is a light orange-yellow insoluble compound which, when heated to 100° C., loses all its combined water and becomes anhydrous. The compound is completely soluble in solutions of sodium or potassium hydroxide and in aqueous ammonia, and in this latter property it differs from zinc ferrocyanide, which is quite insoluble. It also differs from the latter body in being completely decomposed by solutions of the alkali metal carbonate. This difference in properties of the zinc salts may be utilized as a means for the separation of ferrocyanide from ferricyanide.

The precipitate of zinc ferricyanide obtained from potassium ferricyanide is of a much deeper orange

colour and loses 20 per cent. of water when dried over calcium chloride, whereas the compound obtained from the calcium salt loses nothing when treated in a similar manner. The precipitate contains combined potassium and becomes anhydrous at 100° C.

THE CARBONYLFERROCYANIDES

These complex iron cyanogen compounds were first noticed by Orthlieb and afterwards by Mahlar, but they were closely studied by Müller, who has shown that they can be prepared from ferrocyanides. A solution of a ferrocyanide is heated to 135° C. in an atmosphere of carbon monoxide for two or three days, when a portion of the ferrocyanide is converted into the carbonylferrocyanide. This reaction is stated to be as follows :

$$K_4Fe(CN)_6 + CO + 2H_2O = K_3Fe(CN)_5CO + NH_3 + KHCO_3.$$

The reaction is, however, incomplete as a reverse action sets in thus :

$$4K_3Fe(CN)_5CO + 4H_2O = 3K_4Fe(CN)_6 + 4CO + Fe(HCO_2)_2 + 2NH_3.$$

An improvement on this process has been proposed by M. Casaubon,[1] whereby the carbonylferrocyanides are prepared by the action of strong sulphuric acid on ferrocyanides.

Some powdered ferrocyanide is put into a small dish, strong sulphuric acid added sufficient to make a thick pasty mass, and the whole then gently heated : violent effervescence takes place owing to the evolution of carbon monoxide and sulphur dioxide. If now the reaction is stopped at this stage, carbonylferrocyanides will be found in the mixture, the carbon monoxide formed by the decomposition of some of the ferrocyanide reacts with the ferrocyanogen radicle, one carbonyl group taking the place of one cyanogen

[1] *Ann Cong. Soc. Tech.* (1905).

group. The carbonylferrocyanide is more stable to concentrated sulphuric acid than the ferrocyanide.

The carbonylferrocyanides exist in spent oxide of iron and in "cyanogen mud" products obtained in the purification of coal gas, and may be recovered fairly easily from the crude mother liquor resulting from the working up of these two purification products, for the production of sodium or potassium ferrocyanide.

This crude liquor will contain besides ferrocyanides and carbonylferrocyanides, varying quantities of alkaline carbonate, thiocyanate, sulphate, thiosulphate, and sometimes sulphide.

To recover the carbonylferrocyanide from the crude liquor, the solution must be evaporated down to a sp. gr. of 1150 and left to cool, when the bulk of the ferrocyanide in solution will be deposited as crystals, leaving the carbonylferrocyanides, the sodium and potassium salts of which are more soluble than the corresponding ferrocyanides in solution. The clear liquor is then poured off the crystals, diluted with water, rendered just acid with hydrochloric or dilute sulphuric acid and precipitated with a solution of ferric chloride or sulphate. A dark blue or purple-violet precipitate results, consisting of the mixed iron salts of ferrocyanide and carbonylferrocyanide, which must be filtered off and washed free from soluble salts, whereby the latter body is freed from all impurities except ferrocyanide.

When the mixed iron compounds are thoroughly washed, they are converted into their calcium salts by boiling with lime and filtering the liquor from the excess lime and ferric hydroxide.

If the original crude liquor contained potassium salts, the filtered solution of the calcium compounds, obtained as above, should be evaporated to about 1.2 sp. gr. and cooled; any potassium retained by the precipitated iron compounds will be deposited as the sparingly soluble calcium potassium ferrocyanide.

The amount of ferrocyanide in the liquor is then

determined, and the calcium salts in a portion of the liquor converted into the ammonium compounds by precipitation with ammonium carbonate. The amount of solution thus treated should be sufficient, that when subsequently mixed with the bulk of the liquor and boiled enough ammonium salts are present to precipitate all the ferrocyanide as the sparingly soluble calcium ammonium ferrocyanide, rendered practically insoluble by the excess of calcium and ammonium salts, and the clear liquor filtered from the precipitate without washing.

The filtered liquor is then boiled with slaked lime to displace any excess of ammonia, filtered and evaporated to obtain crystals of the calcium salt which may be purified by recrystallization.[1]

The sodium, potassium and ammonium salts are readily prepared from the calcium salt by precipitating the calcium from solution with the respective carbonates. From the solution of the ammonium salt, the barium and strontium compounds are prepared by boiling off the ammonia with barium or strontium hydroxide and the excess of alkaline earth hydroxide removed by passing a stream of carbon dioxide through the solution. From the barium salt, the magnesium and lithium compounds may be prepared, by precipitation with the corresponding sulphates.

The carbonylferrocyanides of the heavy metals, which for the most part are insoluble in water, are prepared in a pure condition by precipitating a solution of the calcium salt with the chloride or nitrate of the heavy metal.

The salts of the alkali and alkaline earth metals, including lithium and magnesium, when pure are of a pale yellow colour. They are all very soluble in water, but are insoluble in alcohol, and several of them are deliquescent.

Most of the salts of the heavy metals are insoluble in water, but solutions of lead, stannic, chromic or aluminium salts produce no precipitate.

[1] H. E. Williams, *P.C.S.*, **29**, 10.

The most characteristic reaction of the carbonylferrocyanides by which they can be readily distinguished from the ferrocyanides and other iron cyanogen compounds is the beautiful violet coloured precipitate produced by the addition of a solution of a ferric salt.

Ferrous solutions produce a white precipitate which rapidly oxidizes to violet when exposed to the air, and a solution of a cupric salt precipitates the green cupric compound from solutions of the carbonylferrocyanides similar in appearance to cupric ferricyanide.

Some slight decomposition occurs when solutions of the soluble carbonylferrocyanides are repeatedly boiled or evaporated, and a small deposit of ferric hydroxide forms. This slight decomposition takes place to a somewhat greater extent in the solutions of the lithium, magnesium and the ammonium salt, but the latter is much more stable than the corresponding ferrocyanides, as the solution may be evaporated down to the crystallizing point with but slight decomposition occurring.

As in the case of the ferrocyanides a calcium potassium salt is known, which though moderately soluble in water is much less soluble than either of its constituent carbonylferrocyanides. It is only sparingly soluble in cold solutions containing an excess of potassium and calcium salts. A similar but more soluble calcium ammonium salt may also be prepared.

On prolonged exposure to strong sunlight, the solution and also the crystals of several of the soluble carbonylferrocyanides, particularly the calcium salt, are slowly decomposed and turn blue from the formation of a trace of ferrocyanide.

The carbonylferrocyanides resist the action of concentrated sulphuric acid to a much greater extent than do the other iron cyanogen compounds, and some carbonylferrocyanide can still be detected undecomposed after heating for some time. But when heated after the further addition of potassium sulphate, decomposition rapidly takes place, carbon dioxide, carbon monoxide and sulphurous acid gases are evolved with effervescence, with formation of the

sulphates of iron, ammonium and the base of the carbonylferrocyanide.

Boiled with a solution of ammonium or potassium persulphate, the carbonylferrocyanide are completely decomposed, the iron being converted into a basic sulphate. This decomposition is much more difficult than with the ferrocyanides, the solution first turning deep violet and then gradually decomposes on boiling.

The insoluble heavy metal salts, when prepared from the alkali metal carbonylferrocyanides, contain a considerable proportion of the alkali metal in combination, and a large number of these compounds may be prepared varying according to the particular alkali metal salt taken, and with the method of precipitation employed. The alkaline earth metal carbonylferrocyanides have but little tendency to form these complex salts, and the heavy metal precipitates obtained from these solutions are generally free from combined alkaline earth metal. The precipitates containing alkali metal in combination differ slightly in appearance from the pure product as they are generally darker in colour, and when dry form hard vitreous masses.

The insoluble salts of copper, cobalt, cadmium, nickel and zinc are soluble in aqueous ammonia, and are redeposited from this solution on exposure to the air in combination with ammonia.

Like the ferrocyanide compounds, the insoluble carbonylferrocyanides, when air-dried, still contain a considerable proportion of water held in combination: some of this water is yielded up when they are exposed to a dry atmosphere, such as over calcium chloride or concentrated sulphuric acid, and a further quantity is lost when they are heated to 100° C. If exposed to the air after this treatment most of these compounds reabsorb moisture from the atmosphere; in some cases only the water lost at 100° C. is absorbed, while in others the water lost at 100° C. and also all the water lost in drying over calcium chloride is exactly reabsorbed. The cobalt salt changes colour from reddish-pink to violet when water is driven off by heat, but changes

back to its original colour on exposure to the air with reabsorption of the water lost.

THE METALLIC CARBONYL-FERROCYANIDES

AMMONIUM CARBONYLFERROCYANIDE, $(NH_4)_3Fe(CN)_5CO3H_2O$, is a very soluble salt which separates out in yellow crusts of microscopic crystals on evaporating the concentrated solution over sulphuric acid. It is much more stable than the corresponding ferrocyanide, and the solution can be evaporated with practically no decomposition. At 100° C. it loses 1 molecule of water, but is otherwise unchanged. Many of the substituted ammonias form sparingly soluble salts, thus the dimethylaniline salt, $[C_6H_5N(CH_3)_2]_3H_3Fe(CN)_5CO8H_2O$, separates in sparingly soluble light yellow crystals : the diethylaniline salt, $[C_6H_5N(C_2H_5)_2]_3H_3Fe(CN)_5CO.3H_2O$, is also sparingly soluble and similar in appearance to the above. The pyridine salt is moderately soluble. These organic ammonia salts differ from the corresponding ferrocyanides in that they are neutral salts, whereas the ferrocyanides are acid salts. Thus dimethylaniline ferrocyanide contains two unsaturated hydrogen atoms :

$$[C_6H_5N(CH_3)_2H]_2H_2Fe(CN)_6.$$

BARIUM CARBONYLFERROCYANIDE, $Ba_3[Fe(CN)_5CO]_2 14H_2O$, is an exceedingly soluble salt which crystallizes with difficulty in light yellow, almost white, crusts. When heated to 100° C., it loses 3 molecules of water and does not appear to form double salts.

CALCIUM CARBONYLFERROCYANIDE, $Ca_3[Fe(CN)_5CO]_2 8H_2O$, is a very soluble salt which deliquesces in moist air and loses 1 molecule of water at 100°C. With the salts of potassium it forms the double calcium potassium compound, $CaKFe(CN)_5CO5H_2O$, which crystallizes well and is only moderately soluble in water, much less so than the calcium and potassium

salts separately. Like the corresponding double ferrocyanide, it is less soluble in solutions containing an excess of calcium and potassium salts. The double calcium ammonium carbonylferrocyanide can also be prepared, but it is more soluble than the preceding.

CADMIUM CARBONYLFERROCYANIDE, $Cd_3[Fe(CN)_5CO]_27H_2O$, is prepared by precipitating a solution of the calcium salt with a cadmium salt. When air-dried the compound forms a white insoluble powder containing 20 molecules of water, thirteen of which are lost when dried over calcium chloride, and the whole of the remainder when heated to 100° C., but when exposed to the air for some hours it reabsorbs 7 molecules of water. The white precipitate readily dissolves in aqueous ammonia, from which it separates as the ammonia evaporates in small well-defined, yellow crystals of the composition:

$$Cd_3[Fe(CN)_5CO]_26NH_3.$$

COBALT CARBONYLFERROCYANIDE, $Co[Fe(CN)_5CO]_218H_2O$, is a reddish-pink precipitate which retains 18 molecules of water when dried over calcium chloride. Heated to 100° C. it loses 13 molecules of water, the colour changing to violet. On exposure to air it then reabsorbs all water lost on heating to 100° C., the colour at the same time changing from violet to its original colour. If prepared from the carbonylferrocyanides of the alkalis the precipitate contains combined alkali metal. The compound prepared by adding an excess of cobalt chloride solution to a solution of potassium carbonylferrocyanide, dried after thorough washing over calcium chloride, forms hard vitreous masses of a dark purple colour of the composition agreeing with the formula $Co_5K_2[Fe(CN)_5CO]_430H_2O$, which retains 8 molecules of water when heated to 100° C., the compound at the same time turning blue. Like the pure cobalt salt it reabsorbs water on exposure to air and reverts to its original colour.

CUPRIC CARBONYLFERROCYANIDE, $Cu_3[Fe(CN)_5CO]_2 14H_2O$, when prepared from the calcium salt by precipitation, washed and dried, forms a light green loose insoluble powder, unaltered by boiling hydrochloric acid. The air-dried product loses water equivalent to 7 molecules when exposed to a dry atmosphere, such as over calcium chloride, and has then the composition expressed above. When heated to 100° C. a further 7 molecules of water are driven off, the compound at this temperature still retaining 7 molecules of water; when subsequently exposed to the atmosphere 7 molecules of water are reabsorbed. The green precipitate dissolves readily in aqueous ammonia to a deep blue liquid, from which it separates as the ammonia escapes at the ordinary temperature, in dark olive-green crystalline crusts of the composition $Cu_3[Fe(CN)_5CO]_2 3NH_3 9H_2O$. When potassium carbonylferrocyanide is exactly precipitated with a cupric salt, the compound, $Cu_7K_4[Fe(CN)_5CO]_6 \times H_2O$, separates, which is much darker in colour than the pure cupric salt described above. It dries to a hard vitreous mass.

When the pure cupric salt is boiled with strong nitric acid (sp. gr. 1.42) it is partially oxidized and some copper is extracted. The compound then has a composition agreeing with the formula, $Cu_5[Fe(CN)_5CO]_4 30H_2O$, which appears to be a compound of cupric carbonylferro and carbonylferricyanide:

$$Cu_5[Fe(CN)_5CO]_4 = Cu_3[Fe''(CN)_5CO]_2 ; 2CuFe'''(CN)_5CO,$$

similar to the bronze-coloured oxidation products of the platinocyanides. The above compound, when treated with a warm solution of potassium carbonate, is partly dissolved, and on filtering a greenish solution is obtained, from which a yellowish-green precipitate is produced on neutralization with hydrochloric acid, and a precipitate of black cupric oxide when the green solution is boiled. Similar compounds have been obtained by J. A. Müller [1] by the action of chlorine on the potassium salt.

[1] *Bull Soc. Chim.* (1903), iii. **29**, 1161–1166.

FERRIC CARBONYLFERROCYANIDE, $Fe'''Fe(CN)_5CO5H_2O$, is precipitated pure from the calcium salt solution as a gelatinous precipitate of a beautiful violet colour. When washed and dried it forms a dark, almost black, granular powder with a bronze lustre and grinds to a dark violet powder. When precipitated from the alkali salts it retains small portions of the alkali metal combined. It is quite insoluble in water and is unattacked by boiling hydrochloric acid, and when heated to 100° C. it loses 2 molecules of water. When heated with strong nitric acid, a violent oxidizing action takes place and a compound is then formed which when washed free from acid forms a beautiful violet colloidal solution with water.

FERROUS CARBONYLFERROCYANIDE is formed as a white precipitate which rapidly oxidizes to violet on exposure to the air or when treated with oxidizing agents.

HYDROCARBONYLFERROCYANIC ACID, $H_3Fe(CN)_5COH_2O$. If a moderately strong solution of a carbonylferrocyanide is acidified with hydrochloric acid and shaken with ether, waxy looking lumps with a faint yellow tinge separate slowly out. The acid is quite stable in the air and can be dried without decomposition. At 100° C. it loses half a molecule of water and slightly decomposes. It is a fairly strong acid and decomposes carbonates with effervescence.

LITHIUM CARBONYLFERROCYANIDE, $Li_3Fe(CN)_5CO4H_2O$, may be easily prepared by exactly precipitating a solution of the barium salt with sulphate of lithium. The salt separates from the cooled concentrated solution in small pale yellow, very deliquescent crystals, which are very soluble in water. When heated to 100° C., 2 molecules of water are evolved. If the solution of the salt is repeatedly boiled, slight decomposition occurs and a trace of ferric oxide is formed suspended in the liquid.

MAGNESIUM CARBONYLFERROCYANIDE, $Mg_3[Fe(CN)_5CO]_216H_2O$. This salt is prepared, like the

preceding, from the barium salt and magnesium sulphate by double decomposition. It is a very soluble salt, which crystallizes with difficulty in pale yellow crystals which effloresce slightly when exposed over calcium chloride, and lose 10 molecules of water at 100° C. The solution decomposes slightly on continued boiling.

MANGANESE CARBONYLFERROCYANIDE, $Mn_3[Fe(CN)_5CO]_2 18H_2O$, is obtained in the pure state by precipitation from a solution of the calcium or hydrogen salt by manganese chloride. It is a white insoluble compound which retains 4 molecules of water at 80° C., one of which it loses when the temperature rises to 100° C. When the dry compound is boiled with strong nitric acid (sp. gr. 1.42), energetic oxidation takes place with formation of a deep brown granular powder having the composition $Mn_5[Fe(CN)_5CO]_4 \cdot 26H_2O$. This compound may be a mangano-manganic carbonylferrocyanide, but is more probably a manganous carbonylferro carbonylferricyanide similar to the cupric salt described above, thus :

$$Mn_5[Fe(CN)_5CO]_4 = Mn_3[Fe''(CN)_5CO]_2 : 2MnFe'''(CN)_5CO.$$

When digested in a neutral solution of a carbonylferrocyanide, the brown compound is changed into the white manganous carbonylferrocyanide, while the solution becomes deep yellow. When decomposed with alkaline hydroxides it is decomposed into a soluble carbonylferrocyanide and a brown mixture of manganomanganic and manganous hydroxide :

$$3Mn_5[Fe(CN)_5CO]_4 + 36KOH = 12K_3Fe(CN)_5CO + 3Mn_3O_4 + 6MnO + 18H_2O.$$

MERCURIC CARBONYLFERROCYANIDE. When a solution of mercuric chloride is added to a carbonylferrocyanide solution a white precipitate is first formed, which soon decomposes and becomes contaminated with the violet iron salt.

MOLYBDENUM CARBONYLFERROCYANIDE. The addition of an acid solution of ammonium molybdate to a carbonylferrocyanide solution forms a dark brown

precipitate soluble in excess of the carbonylferrocyanide solution to a reddish-brown colour.

NICKEL CARBONYLFERROCYANIDE, $Ni_3[Fe(CN)_5CO]_2 13H_2O$, precipitated from a solution of the calcium salt, is a gelatinous apple green precipitate similar in appearance to the ferrocyanide. When washed and dried it forms a hard green vitreous mass. When thoroughly air-dried the compound contains water equivalent to 19 molecules, six of which it loses when dried over calcium chloride and a further six molecules when heated to 100° C. If then exposed to the atmosphere it reabsorbs all the water lost at 100° C. together with that lost on exposure to calcium chloride, and has then exactly the same weight and percentage composition as the original air-dried sample.

The compound dissolves in ammonia solution to a light blue liquid, which when exposed to the air deposits the salt, $Ni_3[Fe(CN)_5CO]_2 2NH_3 4H_2O$, as a white powder with a slight blue tinge. When the dried powder is boiled with nitric acid (1.42 sp. gr.) it is at first violently attacked and a dark brown salt is obtained of a composition which agrees with the formula, $Ni_5[Fe(CN)_5CO]_4 27H_2O$, which is probably a carbonylferro-carbonylferricyanide of nickel.

The nickel compound prepared by precipitating a solution of the potassium salt is very finely divided and difficult to filter and contains potassium in combination.

POTASSIUM CARBONYLFERROCYANIDE, $K_3Fe(CN)_5CO.H_2O$, may be prepared from the barium or calcium salt by double decomposition with potassium carbonate or from the barium salt with potassium sulphate. This salt is one of the few soluble carbonylferrocyanides that crystallize well. The crystals lose their combined water and become anhydrous at 100° C.

SILVER CARBONYLFERROCYANIDE, $Ag_3Fe(CN)_5CO$, is obtained as a white insoluble clotty precipitate.

SODIUM CARBONYLFERROCYANIDE, $Na_3Fe(CN)_5CO6H_2O$, is prepared like the potassium salt by precipitating the barium salt solution with sodium

carbonate or sulphate. It is a very soluble salt which crystallizes well in yellow prismatic needles. When heated to 100° C. the crystals turn white and become anhydrous, but when exposed to the air they are slightly deliquescent.

STANNIC CARBONYLFERROCYANIDE. Stannic chloride added to calcium carbonylferrocyanide produces no precipitate, only a reddish coloration. On dilution and warming a thick gelatinous precipitate of stannic hydrate is produced. Stannous salts produce a precipitate of a white basic salt.

STRONTIUM CARBONYLFERROCYANIDE, $Sr_3[Fe(CN)_5CO]_2 10H_2O$, is prepared by boiling a solution of the ammonium salt with an excess of strontium hydroxide, and removing the excess of the latter by carbon dioxide. It is a very soluble salt which crystallizes in small deliquescent crystals, which lose 2 molecules of water at 100° C.

URANIUM CARBONYLFERROCYANIDE is produced as a dark red-brown precipitate by adding a solution of uranium acetate to a solution of a carbonylferrocyanide. It is very similar to the ferrocyanide in colour.

ZINC CARBONYLFERROCYANIDE, $Zn_3[Fe(CN)_5CO]_2 7H_2O$, is a white insoluble precipitate which loses 4 molecules of water at 100° C. It dissolves in ammonia solution to a clear solution, which on exposure to the air deposits an ammonia compound as a white powder of the composition $Zn_3[Fe(CN)_5CO]_2 4NH_3 4H_2O$. Zinc carbonylferrocyanide is completely soluble in caustic soda or potash solution, and is decomposed by the carbonates of sodium and potassium.

THE NITROFERRICYANIDES

When a finely powdered and soluble ferrocyanide is heated to 100° C. with moderately strong nitric acid, a part of the ferrocyanide is completely decomposed, giving rise to a variety of oxidation products such as cyanogen, oxamide, hydrocyanic acid, ammonia, etc.,

and the remainder is first oxidized to ferricyanide and then one-sixth of the cyanogen is replaced by the group nitrosyl [NO], giving rise to a new class of compounds having the general formula, $M_2Fe(CN)_5NO$.

From the soluble ferricyanides, the nitroferricyanides may be produced by the action of sodium nitrite and acetic acid (Städler), preferably in the presence of a little mercuric chloride, thus :

$$2K_3Fe(CN)_6 + 4NaNO_2 + 2HC_2H_3O_2 + HgCl_2 = 2Na_2Fe(CN)_5NO + Hg(CN)_2 + 2KCl + 2KC_2H_3O_2 + KNO_3 + KNO_2 + H_2O.$$

If the calcium salt is taken and sodium nitrite added the nitrous acid may be set free by passing carbon dioxide through the solution.

Nitroferrocyanides also result when the double ferrous cyanide produced by the exact precipitation of ferrous sulphate with potassium cyanide solution is added to a solution of potassium or sodium nitrite :

$$5KCN + 2FeSO_4 = KFe_2(CN)_5 + 2K_2SO_4,$$

and

$$KFe_2(CN)_5 + KNO_2 = K_2Fe(CN)_5NO + FeO.$$

The sodium salt may also be prepared by adding a concentrated solution of ferrous sulphate to a solution of equal parts of potassium or sodium cyanide and sodium nitrite ; brisk effervescence of gases takes place with formation of ferric oxide ; the mixture is allowed to stand five hours in the cold, then just made alkaline, warmed and filtered and the nitroferricyanide separated by evaporation.[1]

Small quantities of nitroferricyanide are formed when insoluble ferrocyanides are oxidized by nitric acid, such, for example, as the manganese and lead compounds. The latter body when added to warm dilute nitric acid so long as it dissolves forms some considerable quantities of nitroferricyanides.

The nitroferricyanides are generally prepared by the action of nitric acid on a soluble ferrocyanide, and as

[1] Hofmann, *Z. anorg. Chem.* (1889), **10**, 262.

the sodium salt crystallizes much better than the potassium salt, it is usual to prepare the former.

The method is carried out as follows : 48.5 grm. of crystallized sodium ferrocyanide are ground and placed in a flask of 1000 c.c. capacity, and 250 c.c. of dilute nitric acid (1 : 1) added and the action allowed to proceed in the cold under a hood in a good draught. When the first action is over the mixture, which has now become a dark brown liquid, is heated to 100° C. on a water-bath until a drop of the liquid produces neither a blue nor a green coloration with a solution containing a mixture of ferrous and ferric salts. The liquid is diluted conveniently and neutralized with precipitated calcium carbonate, filtered, and the solution evaporated and put aside to crystallize. Large crystals of sodium nitroferricyanide are obtained sometimes contaminated with a little of the calcium salt. They may be easily purified by recrystallization in hot water, any calcium present in solution removed by exact precipitation with sodium carbonate and the filtered solution crystallized.

The solutions of the soluble nitroferricyanides in water are on the whole fairly stable. The sodium and potassium salts can be evaporated without decomposition, and the barium, strontium and calcium salts with but slight decomposition, though it is better to evaporate them under reduced pressure, some hydrocyanic acid being evolved and a little ferric hydroxide precipitated, but prussian blue is seldom deposited if the solutions are pure.

The nitroferricyanides of the alkali and alkaline earth metals, including lithium and magnesium, are all soluble in water, and crystallize in fine ruby-red crystals. The sodium, calcium and barium salts crystallize exceedingly well, particularly the two latter. Many of the salts of the heavy metals produce precipitates which are in most cases of a pink colour ; chromic, ferric, aluminium, stannic, bismuth, cerium, thorium and mercuric salts produce no precipitate.

A nitroferricyanide solution when heated with

sodium or potassium hydroxide is decomposed, the colour of the solution first changing to orange, then yellow, and finally ferric hydroxide is precipitated and a solution of sodium nitrite and ferrocyanide is left :

$$6Na_2Fe(CN)_5NO + 14NaOH = 5Na_4Fe(CN)_6 + FeO + 6NaNO_2 + 7H_2O.$$

The ferrous hydroxide is immediately oxidized by the nitrite thus :

$$6FeO + NaNO_2 + 2H_2O = 3Fe_2O_3 + NaOH + NH_3,$$

or expressed in one equation :

$$36Na_2Fe(CN)_5NO + 83NaOH = 30Na_4Fe(CN)_6 + 3Fe_2O_3 + 35NaNO_2 + 40H_2O + NH_3.$$

This reaction is quantitative, the whole of the cyanogen being left in combination as ferrocyanogen, and no nitrogen is evolved as gas.

Nitroferricyanides in solution yield a beautiful deep violet coloration with a small quantity of an alkaline sulphide. This reaction is remarkably sensitive and is frequently made use of in analytical chemistry for the detection of a trace of either nitroferricyanide or an alkaline sulphide. The colour, however, is transient and rapidly decomposes.

When hydrogen sulphide is passed for some hours through a solution of sodium nitroferricyanide heated on the water-bath, decomposition of the compound takes place, hydrocyanic acid is evolved and a precipitate of sulphur, and an iron cyanogen complex is formed which becomes blue on exposure to the air, while a ferrocyanide and a nitrosulphide are left in solution.[1]

Nitroferricyanides are reduced by sodium amalgam forming ferrocyanides and ammonia.[2]

$$12Na_2Fe(CN)_5NO + 8Na_2 + 54H = 10Na_4Fe(CN)_6 + 12NH_3 + Fe_2O_3 + 9H_2O.$$

[1] D. Venditori, *Atti R. Accad. Lincei* (1913), [v] **22**, i, 162–67 ; *J.C.S.*, *A*. 1 (1913), 451.

[2] K. Bhaduri, *Z. anorg. Chem.* (1913), **84**, 95–6.

When reduced in neutral solutions with a copper zinc couple nitrogen is formed :[1]

$$4Na_2Fe(CN)_5NO + 5H_2 = 2Na_4Fe(CN)_6 + 8HCN + 2N_2 + H_2O + Fe_2O_3.$$

Sulphuric acid and sodium amalgam yield prussian blue and hydrocyanic acid :

$$4Na_2Fe(CN)_5NO + 16H_2SO_4 + 11Na_2 = 2FeNaFe(CN)_6 + 2(NH_4)_2SO_4 + 4H_2O + 14Na_2SO_4 + 8HCN.$$

When ignited with concentrated sulphuric acid complete decomposition occurs, forming the sulphates of iron, ammonium and the sulphate of the base of the nitroferricyanide. They are also decomposed in solution by boiling with ammonium or potassium persulphate.

Acetone gives a red colour with a solution of a nitroferricyanide accompanied by the production of oximinoacetone.[2] Similar colorations are yielded with other ketones and aldehydes ranging from yellow-red to violet. With creatine in presence of caustic alkali a fine ruby-red coloration is produced changing to straw-yellow.

When strong sodium nitroferricyanides solution is saturated in the cold with ammonia and kept twenty-four hours, the whole of the nitroferricyanide enters into the reaction and the compound **disodium ammonium ferropentacyanoammonia,** $Na_2NH_4[Fe(CN)_5NH_3]\text{-}2H_2O$, is obtained, the iron being reduced from ferri to ferrous :[3]

$$Na_2[Fe(CN)_5NO] + 3NH_3 + H_2O = Na_2NH_4[Fe(CN)_5NH_3] + NH_4NO_2.$$

If the crystalline precipitate is filtered off before the whole of the nitroferricyanide has entered, the reaction **ferropentacyanoammonia sodium** is obtained,

[1] K. Bhaduri, *l.c.*

[2] Livio Cambi, *Atti R. Accad. Lincei* (1913), [v], **22,** i. 376–81.

[3] Manchot, *Ber.* (1912), **45,** 2869–79.

$Na_3[Fe(CN)_5NH_3]6H_2O$ (Hofmann). This compound loses 3 molecules of water when dried over calcium chloride.[1] The salt absorbs carbon monoxide in aqueous solutions, the ammonia being replaced by CO; it also slowly absorbs oxygen, the iron being oxidized to the ferric state.

The nitrosyl group can also be replaced by alkylamines giving rise to compounds which yield similar reactions, and combine with carbon monoxide and oxygen. The following compounds have been prepared and described by W. Manchot and P. Woringen.[2]

TRISODIUM FERROPENTACYANOMETHYLAMINE, $Na_3[Fe(CN)_5NH_2CH_3]$, is obtained as yellow crystals by the action of methylamine on sodium nitroferricyanide in methyl alcohol solutions.

DISODIUM FERROPENTACYANOETHYLENEDIAMINE, $Na_2[Fe(CN)_5C_2H_4(NH_2)_2]$, is difficult to obtain pure.

Pyridine does not react on sodium nitroferricyanide, but when added to a methyl alcoholic solution of disodium ammonium ferropentacyanoammonia, the compound **trisodium ferropentacyanopyridine,** $Na_3[Fe(CN)_5C_5H_5N]$, is obtained as a mass of long yellow needles.

Aromatic amines such as aniline and toluidines do not appear to react with sodium nitroferricyanide.

When boiled with ammoniacal silver nitrate nitroferricyanides are completely decomposed, ferric oxide is precipitated, and a double silver ammonium cyanide is left in solution.

If a concentrated solution of 6 grm. of hydrazine hydrate is added slowly to an ice-cold alkaline solution of 12 grm. of sodium nitroferricyanide in ethyl or methyl alcohol, a yellow crystalline precipitate is obtained of the compound **sodium pentacyanohydrazinoferrite** (hydrazinoferropentacyanide), $Na_3N_2H_4Fe(CN)_5H_2O$, which gives the characteristic reactions of a ferropentacyanide, but it readily decomposes. Similar

[1] Manchot, *l.c.*

[2] *Ber.* (1913), **46**, 3514–21; *J.C.S.*, i. 1311 (1913).

products may be obtained, but with more difficulty, with phenylhydrazine, ethylamine, and diethylamine.[1]

METALLIC SALTS

Ammonium nitroferricyanide is easily prepared by decomposing the barium salt solution with ammonium sulphate and evaporating the solution over sulphuric acid. It crystallizes in ruby-red crystals, and it is fairly stable in the solid state and in solution, but the latter decomposes on boiling.

Barium nitroferricyanide, $BaFe(CN)_5NO\text{-}H_2O$, may be prepared in a state of purity by boiling the recently precipitated zinc compound with precipitated barium carbonate and evaporating the filtrate under reduced pressure: it crystallizes in fine large ruby-red crystals. The cadmium salt is an insoluble pink precipitate which is soluble in ammonia and excess of hydrochloric acid. The calcium salt, $Ca[Fe(CN)_5NO]\text{-}4H_2O$, may be readily prepared by the action of nitric acid on calcium ferrocyanide, and then neutralizing the excess acid with calcium carbonate, when the action is complete. It crystallizes very well in dark red prisms which lose 3 molecules of water at 100° C. The cobalt salt is an insoluble bright pink powder soluble in ammonia, but insoluble in hydrochloric acid. The copper salt is a light blue insoluble precipitate readily soluble in ammonia and hydrochloric acid. Ferric salts produce no precipitate when added to a solution of a nitroferricyanide, but a pale pink precipitate is obtained by the addition of a ferrous salt. Lithium nitroferrocyanide is a very soluble salt, and is obtained from the barium salt by double decomposition with lithium sulphate. The magnesium salt is very soluble and is obtained in a similar manner. Manganese nitroferricyanide is an insoluble pink powder which is unattacked by strong nitric acid. The nickel salt is a grey precipitate soluble in aqueous

[1] E. Biesalski and Hauser, *Z. anorg. Chem.* (1912), **74**, 384–88.

ammonia to a reddish-brown solution but is insoluble in nitric acid. Silver nitrate precipitates an insoluble reddish-pink precipitate which dissolves in aqueous ammonia to a red solution. The sodium salt, $Na_2Fe(CN)_5NO2H_2O$, is obtained by the general method described above. It crystallizes well and does not lose water at 100° C. The zinc salt is obtained as a pink precipitate readily soluble in ammonia and in excess of hydrochloric acid.

PERFERRICYANIDES

It has been known for some time that on the addition of iodine to a strong solution of potassium ferricyanide or ferrocyanide, the mixture being warmed gently, a reaction takes place and the solution becomes very dark-coloured, almost black : if now alcohol is added, a crystalline salt, almost black in colour, is precipitated, which may be purified by resolution in water and reprecipitation with alcohol. The solution in water is deep violet, but the compound is very unstable, and rapidly decomposes, evolving cyanogen,[1] and when boiled, potassium ferricyanide is regenerated and ferric oxide precipitated.

The freshly prepared aqueous solution gives green precipitates with most metallic salt solutions including zinc, the ferrocyanide of which is white, and the ferricyanide orange. When the salt is treated with nitrous acid, nitroferricyanides are formed.

The acid has not been isolated, but it is considered to be dibasic, and it acts as an energetic oxidizer.

The compound is also said to be formed when chlorine in excess is passed through potassium ferrocyanide solution, or when a solution of potassium ferrocyanide is mixed with potassium chlorate, and acidulated with hydrochloric acid. After the disengagement of gases has ceased, the solution is neutralized carefully with sodium carbonate, and the perferri-

[1] Skraup, *A.*, **189**, 368.

cyanide or "black prussiate" precipitated by the addition of alcohol.

The almost black crystals obtained by reprecipitation by alcohol were considered by Bong [1] to have a composition agreeing with the formula, $K_2Fe(CN)_6$. This formula was accepted as probably correct by Skraup,[2] although the figures obtained by him for the iron and carbon were in the ratio of 1 : 5.

The discovery of sodium aquopentacyanoferrite by Hofmann [3] threw some considerable doubt on the formula of Bong for the so-called perferricyanide. The latter salt exhibits reactions which correspond to those of the pentacyanoferrites. Livio Cambi [4] found that in an analysis of the compound prepared according to Skraup's method and purified several times, that the ratio of potassium to iron was as 2 : 1, and that only one atom of iodine was liberated by hydriodic acid for each atom of iron in the compound. Two however should be liberated if the generally accepted formula of Bong was correct, thus :

$$H_2Fe(CN)_6 + 2HI = H_4Fe(CN)_6 + I_2.$$

He suggests that the formula is $K_2Fe(CN)_5$, and that the reaction may be expressed :

$$K_3Fe(CN)_6 + Cl_2 = K_2Fe(CN)_5 + KCl + CNCl.$$

This formula for the salt is in agreement with the values obtained by Skraup for the ratio of iron to carbon, and would also seem to be confirmed by the statement that an almost theoretical yield of cyanogen chloride may be obtained in the preparation of the compound.

The substitution of sodium ferrocyanide for the potassium salt yielded the corresponding sodium salt identical with the compound obtained by Hofmann from sodium nitroferricyanide.[5]

[1] *J.C.S.* (1876), i. 907.
[2] *J.C.S.* (1877), **32**, 597.
[3] *J.C.S.* (1900), i. 591.
[4] *Gazz.* (1911), **41**, i. 157–66.
[5] *Ann.*, **312**, 18.

Alkaline hydroxylamine, aldehyde, acetone or alkaline sulphides at 0° C. reduce potassium perferricyanide forming potassium aquopentacyanoferrite, $K_3[Fe(CN)_5H_2O]$, which is instantly oxidized to the perferricyanide by bromine.

Excess of potassium sulphite in presence of potassium hydroxide also reduces the salt with formation of potassium ferrosulphitocyanide, $K_3Fe(CN)_5SO_33H_20$, which crystallizes in small yellow prisms from aqueous alcohol, and also exhibits all the reactions of a pentacyanoferrite.

The formation of the black prussiate is therefore considered by Livio Cambi to take place in two stages:

(1) $Fe(CN)_6''' + Cl_2 = Fe(CN)_5Cl + CNCl.$
(2) $(Fe'''(CN)_5Cl)'' + H_2O = (Fe(CN)_5H_2O)'' + Cl.$[1]

[1] *J.C.S.* (1911), i. 430.

CHAPTER VI

OXYCYANOGEN COMPOUNDS

CYANIC, CYANURIC, FULMINIC AND FULMINURIC ACID

CYANIC ACID

THE acid of this series of cyanogen compounds was first discovered by Vanquelin in 1818, who, however, named it cyanous acid, but the compound was more completely investigated by Wöhler some four years later.

The acid may be prepared :

1. By the action of heat on its polymeride, cyanuric acid, $C_3N_3O_3H_3$, which splits up into cyanic acid, HCNO (Wöhler).
2. By heating urea with phosphoric anhydride.
3. By heating uric acid with dilute sulphuric acid and manganese dioxide (Dobereiner).
4. By igniting mercuric urate.

And may be prepared in combination with a base :

5. By passing cyanogen gas into a solution of caustic soda or potash, one half of the cyanogen forming cyanate and the remainder being combined as cyanide :

$$(CN)_2 + 2KOH = KCN + KCNO + H_2O.$$

6. By the electrolysis of a solution of a cyanide whereby cyanate is formed at the anode.
7. By the action of a hypobromite or potassium permanganate on an alkaline solution of a cyanide.

8. The ammonium salt may be produced by subliming urea in a vacuum at 160 to 190° C.[1]

9. It is, however, most conveniently prepared by fusing a dry alkali metal ferrocyanide or cyanide with an easily reducible metallic oxide or oxidizing agent, such as manganese dioxide, red lead, potassium bichromate, etc. :

$$KCN + PbO = KCNO + Pb.$$

The cyanate is recovered by grinding the cooled fused mass and digesting it with hot hydrated alcohol containing 80 per cent. ethylic alcohol and 10 per cent. methylic alcohol. On cooling the filtered alcoholic solution, the cyanate crystallizes out, and the mother liquor can be heated and used for extracting a fresh portion of the melt. It may also be obtained in aqueous solutions as the potassium salt by oxidizing potassium cyanide with potassium permanganate.

Cyanic acid cannot be obtained direct from its salts in the ordinary manner, because at the moment of liberation it takes up water with decomposition. It may, however, be prepared by passing dry hydrochloric acid over silver cyanate and condensing the evolved vapour.[2]

Cyanic acid is a monobasic acid, and forms salts of the type $M'CNO$ and $M''(CNO)_2$, the anhydrous acid is a colourless liquid with a pungent odour suggesting sulphur dioxide or acetic acid. The vapour attacks the eyes, causing a copious flow of tears, and if a drop of the liquid is placed on the hand painful blisters are produced. The anhydrous acid is, however, exceedingly unstable, and rapidly polymerizes into the white insoluble cyamelide, $(CNHO)_3$.

Cyanic acid decomposes in aqueous solutions very rapidly ; in concentrated solutions cyanuric acid is the principal product resulting from the polymerization of the non-ionized cyanic acid. In more dilute

[1] R. Escales, *Chem. Zeit.* (1911), **35**, 595.
[2] Wöhler, *Pogg. Ann.*, v. 386.

solutions the elements of water are taken up with formation of ammonia and carbon dioxide :

$$HCNO + H_2O = NH_3 + CO_2,$$

or of urea and carbon dioxide :

$$2HCNO + H_2O = CO(NH_2)_2 + CO_2.$$

The cyanates of metals which form insoluble carbonates decompose when their aqueous solutions are heated with formation of urea and a carbonate : [1]

$$M''(CNO)_2 + 2H_2O = M''CO_3 + CO(NH_2)_2.$$

The formation of ammonia and carbon dioxide is the only reaction in presence of free mineral acid, while the production of urea and carbon dioxide is the principal reaction when no other acid is present.[2]

The addition of strong hydrochloric acid to a solution of potassium cyanate results in the formation of cyanuric acid, some of the cyanic acid at first formed polymerizing. The addition of acetic acid to a moderately strong solution of potassium cyanate forms a white sparingly soluble crystalline precipitate of potassium hydrogen cyanurate, $KH_2C_3N_3O_3$.

Bromine acts on potassium cyanate solution at the ordinary temperature to produce nitrogen and carbon dioxide, and in solution potassium and ammonium bromide are formed : [3]

$$4KCNO + 4H_2O + 3Br_2 = 4KBr + 2NH_4Br + N_2 + 4CO_2.$$

The cyanates of the alkali metals are quite stable in the solid and dry state, and can be fused without suffering any change.

The cyanates of the alkali and alkaline earth metals are soluble in water, and the salts of the heavy metals are for the most part insoluble, and possess no characteristic colour.

[1] O. and J. Masson, *J.C.S.*, A1, 231 (1910).

[2] C. W. B. Normand and A. C. Cumming, *T.C.S.* (1912), 1852.

[3] Normand and Cumming, *l.c.*

There are two possible isomeric modifications of cyanic acid, viz. normal cyanic acid, HO·C ≡ N, and isocyanic acid, H·N = C : O. The free acid is known in only one form, and difference of opinion still exists as to whether it may be regarded as the normal acid or the isocyanic acid; and the same uncertainty exists with regard to the metallic salts, though they are generally regarded as the isocyanates; the principal chemical difference being that the cyanates are not precipitated by silver nitrate, whereas the isocyanates are completely precipitated.

METALLIC CYANATES

Ammonium cyanate, $(NH_4)CNO$, is difficult to obtain in the free state, for its solution in water is converted into urea on heating or keeping the solution :

$$NH_4CNO = (NH_2)_2CO.$$

All soluble cyanates may thus be converted into urea by evaporating their solutions with ammonium sulphate or chloride. This interesting example of isomeric change was first made known by Wöhler and was the first synthesis of an organic compound. According to R. Exalis,[1] if urea is sublimed in a vacuum at 160° to 190° C., the sublimate consists of solid ammonium cyanate. The salt may be prepared by decomposing the silver salt with ammonium chloride. Barium cyanate, $Ba(CNO)_2$, may be prepared by adding alcohol to a solution of potassium cyanate and barium acetate, or more easily by heating barium cyanurate till it melts, when it is converted into barium cyanate. The salt crystallizes in prisms and its solution decomposes on boiling, with formation of ammonia and barium carbonate :

$$Ba(CNO)_2 + 3H_2O = BaCO_3 + CO_2 + 2NH_3.$$

Calcium cyanate, obtained in solution by passing the vapour of cyanic acid into milk of lime, cannot be

[1] *Chem. Zeit.* (1911), **35**, 595.

separated from its solution by crystallization. This body has been proposed for use as an artificial fertilizer, as it is richer in nitrogen than sodium nitrate. It was to be prepared on a large scale by first passing nitrogen over heated calcium carbide at 2.500° C. in an electric furnace, and then finally oxidized by means of air.[1] Cobalt cyanate is precipitated in combination with the potassium salt in dark blue crystals, $Co(CNO)_2 2KCNO$,[2] by adding cobalt acetate to a solution of potassium cyanate. The addition of a copper salt to a cyanate solution yields a green precipitate of the copper compound; while with lead acetate a white crystalline precipitate is obtained of lead cyanate. It is best to use barium cyanate or potassium cyanate to which some barium nitrate has been added to remove any carbonate. The salt completely decomposes on ignition, and it is slightly soluble in water and in ammonia solutions. From the latter solution it separates combined with ammonia, which it readily loses on exposure to the air. It is fairly stable at the ordinary temperature and may be washed free from impurities, but when boiled with water it is hydrolysed into lead carbonate and urea.[3]

Potassium cyanate, KCNO, is prepared by the methods described above: it is unstable in the moist state and in solution, but may be fused in dry air without decomposition. It is reduced in the fused state by hydrogen, metallic potassium, sodium or carbon with formation of cyanide, and it is readily soluble in water, but insoluble in absolute alcohol. Potassium cyanate combines with cyanamide to form monopotassium amidodicyanate of the formula, $(CN)_2NH_2OK$. Silver cyanate, prepared by precipitation, is a white curdy precipitate insoluble in water, and is anhydrous. It is easily decomposed by warm dilute nitric acid:

$$AgCNO + H_2O + 2HNO_3 = AgNO_3 + NH_4NO_3 + CO_2.$$

[1] *J.S.C.I.*, **15**, 125.
[2] Blomstrand, *J. pr. Chem.* [2], **3**, 207.
[3] *J.C.S.I.*, **22**, 1364.

It is completely decomposed on ignition, leaving a residue of pure metallic silver, and is soluble in ammonia solutions, from which crystals may be obtained of the cyanate combined with ammonia, which, however, is lost on washing with water, or on exposure to the air.

Sodium cyanate is prepared like the potassium salt and is exactly similar in properties.

CYANURIC ACID

NORMAL CYANURIC ACID (tricyanic acid) is a polymeric modification of normal cyanic acid, and occupies the same relation to the latter body as cyanuric bromide, or chloride, does to cyanogen bromide or chloride. It is a tribasic acid, and its constitution is usually represented by the formula, $(CN)_3(OH)_3$.

The acid may be obtained :

1. In the polymerization of pure cyanic acid, together with cyamelide.
2. By the dry distillation of urea :[1]

$$3(NH_2)_2CO = (CN)_3(OH)_3 + 3NH_3.$$

3. By heating cyamelide with concentrated sulphuric acid.[2]
4. By passing chlorine through melted urea.
5. By shaking an aqueous solution of cyanic and hydrochloric acid with ether, the cyanuric acid being dissolved by the ether.[3]

It is, however, conveniently prepared by the method described by R. von Wallher.[4] Ten grm. of urea and 20 grm. of anhydrous zinc chloride are thoroughly mixed and heated to about 220° C. After cooling, the product is treated with dilute hydrochloric acid, and

[1] Scheele, *Opuscula*, **2**, 76 ; Wöhler, *P.*, **15**, 622, etc.
[2] Wellziern, *A.*, **132**, 222.
[3] Klason, *J. pr. Chem.* [2], **33**, 129.
[4] *J. pr. Chem.* (1909), **79**, 126–8.

the separated crystals purified by recrystallization from hot water : 62 per cent. of the theoretical yield of cyanuric acid may be obtained by this process.

Cyanuric acid crystallizes in colourless rhombic prisms combined with 2 molecules of water, which effloresce in air. The acid is exceedingly stable, and dissolves without decomposition in hydrochloric, nitric or dilute sulphuric acid, if the treatment be not too prolonged, but on continued boiling it is decomposed into ammonia and carbon dioxide, and is distinguished by this reaction from cyanic acid, which is immediately decomposed by treatment with acids. With phosphorous pentachloride it reacts to form cyanuric chloride.[1] It is insoluble in alcohol and sparingly soluble in water ; 100 parts of water at 15.5° C. dissolve 2½ parts of the acid, and 4 parts on boiling. When fused with potassium, both potassium cyanide and hydroxide are formed, and on ignition it splits into cyanic acid, which may be recognized by its characteristic odour.

Although cyanuric acid is tribasic, yet the majority of its salts are acid salts. The alkali and alkaline earth metal salts are soluble or sparingly soluble in water, the heavy metal salts being insoluble or but slightly soluble. The alkali metal salts are decomposed on heating into cyanic acid, ammonium cyanate, carbon monoxide, nitrogen, and a cyanate :

$$3MH_2C_3N_3O_3 = 3MCNO + 2HCNO + N_2 + 3CO + NH_4CNO.$$

METALLIC CYANURATES

The ammonium salt, $(NH_4)H_2C_3N_3O_3H_2O$, forms efflorescent prisms, and when heated to 130° C. the ammonia is evolved and a residue of pure acid left. The barium salt, $Ba[H_2(CNO)_3]_2 2H_2O$, may be prepared by adding barium hydroxide to a hot solution of the acid. By adding cyanuric acid to an ammoniacal solution of barium chloride, the salt, $Ba_2[H(CNO)_3]_2$-

[1] Beilstein, *A.*, 116, 357.

$3H_2O$, is obtained as a crystalline precipitate.[1] The compound, $Ca[H_2(CNO)_3]_28H_2O$, crystallizes in colourless needles sparingly soluble in hot water.

The copper salt, $Cu_3(CNO)_6H_2O$, is said to be prepared by the addition of magnesium cyanurate to a copper salt, and the compound, $CuH(CNO)_32H_2O$, by precipitation with the sodium salt. The ammoniacal compounds, $Cu[H(CNO)_3]2NH_3.H_2O$,[2] $Cu[H_2(CNO)_3]_2$-$2NH_3$,[3] and the acid salt, $CuH_2(CNO)_3H_3C_3N_3O_3H_2O$, have been prepared. The lead salt, $PbH(CNO)_33H_2O$, is obtained in microscopic crystals by the addition of the acid to a solution of basic lead acetate. The magnesium salt, $Mg[H_2(CNO)_3]_214H_2O$, has been described by A. Hantzsch.[4] Potassium cyanurate, $KH_2C_3N_3O_3$, is prepared by the addition of hydrochloric acid to a strong solution of potassium cyanate, and is sparingly soluble in water.[5] By dissolving this salt in an excess of potassium hydroxide and then adding alcohol, the salt, $K_2HC_3N_3O_3$, is precipitated, but on treatment with water it decomposes into caustic potash and the preceding salt. The addition of a solution of silver acetate acidified with acetic acid to a solution of the acid, the compound, $AgH_2C_3N_3O_3$, is obtained, whereas if the silver solution is added to a solution of the acid in excess of ammonia, and the precipitate dried at 200° C., the neutral silver salt may be obtained, $Ag_3C_3N_3O_3$.[6] By boiling this salt with potassium hydroxide, the double salt, $Ag_2KC_3N_3O_3$, is produced, and by boiling the lead salt with excess of silver nitrate, the compound, $Ag_4Pb(C_3N_3O_3)_22H_2O$, is formed. The sodium salt, $Na_2HC_3N_3O_3H_2O$, is precipitated in needles by the addition of a large excess of sodium hydroxide to the acid.[7]

[1] Wöhler, *A.*, **62**, 241.
[2] Wöhler, *A.*, **62**, 241.
[3] Wiedermann, *P.*, **74**, 73.
[4] *Ber.* (1906), **39**, 139–53; *J.C.S.* (1906), i. 146.
[5] Liebig and Wöhler, *P.*, **20**, 369; Campbell, *A.*, **28**, 52.
[6] Liebig, *A.*, **26**, 123.
[7] Hantzsch, *l.c.*

CYAMELIDE

When anhydrous cyanic acid is kept it rapidly polymerizes into a white solid substance called cyamelide, $(HCNO)_3$. It is also produced in a similar manner when certain cyanates are treated with concentrated acids.

Cyamelide is a white odourless compound insoluble in hot or cold water, and also in alcohol, ether and dilute acids, and is sometimes called insoluble cyanic acid. When heated it is converted into cyanic acid:

$$(HCNO)_3 = 3HCNO.$$

It is not attacked by boiling hydrochloric or nitric acid, but is completely decomposed by heating with concentrated sulphuric acid, with formation of ammonium sulphate and evolution of carbon dioxide.

It is soluble in ammonia solution and in potassium hydroxide, and from the latter it may be separated as potassium cyanurate.

It has been suggested by Hantzsch,[1] that the constitution of cyamelide may be represented thus:

$$NH : C\begin{<}O \cdot C(:NH)\\ O \cdot C(:NH)\end{>}O$$

its formation from cyanic acid resulting from the union of 3 molecules of the cyanic acid by means of the oxygen atoms, and the above structure is in accordance with its chemical properties and reactions.

FULMINIC ACID

Fulminic acid, $H_2C_2N_2O_2$, has only been obtained in ethereal solutions,[2] by treating sodium fulminate with dilute sulphuric acid at 0° C. The acid separates as a yellow oil which must be immediately dissolved in ether. Fulminic acid rapidly polymerizes to meta-

[1] *Ber.* (1905), **38**, 1016.

[2] Scholvein, *J. pr. Chem.* [2], **32**, 461.

fulminuric acid.[1] Many of the salts of this acid have been prepared which form a class of compounds of the general formula, $M_2C_2N_2O_2$, and are polymeric with the cyanates. The metallic salts, particularly the silver and mercury salts, are characterized by the remarkable property of detonating with great violence when the dry salt is heated or struck, and extreme care should therefore be taken in their preparation.

The mercury and silver salts were first described by Howard,[2] but their composition was first demonstrated by Liebig,[3] and Gay Lussac.[4]

The constitution of these compounds has been the subject of much controversy. Berzelius[5] suggested the formula, $Ag_2O(AgN)_2C_4N_2O_3$, to account for the fact that in the silver salt only half the metal is separated in many of its reactions. In consideration of the method of preparation of these salts, by the action of nitric acid on alcohol in the presence of metallic mercury, Laurent and Gerhardt[6] suggested that they contained the group NO_2, and proposed the formula, $C_2N(NO_2)M''$, which thus brought these compounds into the same class as other explosive nitro compounds. This view was also held by Kekulé, but he subsequently modified it to $CH_2(NO_2)CN$, nitro acetonitril, on account of the comparative ease with which cyanogen compounds could be obtained in some of the reactions of the fulminates, ammonium thiocyanate being one of the products of the action of hydrogen sulphide on the mercury salt.

A number of other formulæ have been proposed by different investigators. Divers[7] proposed :

$$\begin{matrix} HO\cdot CN \\ H\ \ CN \end{matrix}\!\!>O$$

[1] Willard and Hess, *Ber.* (1909), 1346.
[2] *Phil. Trans.*, 1801.
[3] *Ann. Chim. Phys.* [2], **24**, 298.
[4] *Ann. Chim. Phys.* [2], **25**, 285.
[5] Bong, *J.*, **24**, 89.
[6] *Précis de Chimie organique*, **11**, 445.
[7] *C.J.* (1884), 19.

as the constitution of the acid and later the formula :[1]

$$\begin{array}{c} \text{HOCNONC} \\ \quad\quad\quad\

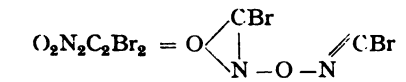
hydrochloric acid, hydroxylamine and formic acid are produced :

$$H_2C_2N_2O_2 + 2HCl + 4H_2O = 2ClH_3NOH + 2H_2CO_2.$$

If the acid is dilute some hydrocyanic acid is also formed.

Mercury fulminate in presence of caustic soda and arsenious oxide yields sodium mercuric cyanide and sodium arsenate.[1]

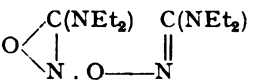
Mercury fulminate treated with bromine in the presence of water yields dibromfuroxan :



to the extent of about 25 per cent. of the fulminate taken.[2]

Treated with aniline it gives aniline black and oxaldianilideoxime, which decomposes at 218° C., and yields a brownish-green colour with ferric salts.

The dibromo compound treated with ammonia forms oxaldiamideoxime, $HON : C(NH_2)C(NH_2) : NOH$, but when the ammonia is replaced by ethylamine oxalbisdiethylamideoxime, $HON \cdot C(NEt_2)C(NEt_2) : NOH$, is obtained in large colourless plates, melting-point 71° C., but it decomposes at 100° C. It is soluble in acids and alkalis, and gives no colour with ferric chloride. Bisdiethylaminofuroxan :



is also formed, together with the preceding compound, from which it may be separated by its insolubility in hydrochloric acid. It is an oil with an odour suggesting camphor and pyridine.

Mercuric chloride and chlorine yield cyanogen chloride and apparently dichlorofuroxan in small quantities.[3]

[1] A. Gutmann, *Ber.*, **42**, 3623–31.

[2] H. Wieland, *Ber.*, **42**, 4192–9.

[3] H. Wieland, *l.c.*

The fulminates heated with aqueous ammonia yield urea, guanidine, and other nitrogen compounds, and when heated with alcoholic ammonia fulminuric acid is obtained.

All the metallic fulminates are intensely explosive in the dry state, and detonate violently when struck. They should be stored only in cardboard or paper boxes with loose-fitting lids.

METALLIC FULMINATES

The mercury or silver salt may be prepared by dissolving silver or mercuric nitrate in excess of dilute nitric acid or the metals may be dissolved in an excess of the acid. This mixture is then added to a large proportion of alcohol. After some little time a violent reaction sets in with rise of temperature which must be kept down by the addition of more alcohol, and on cooling the mixture when the reaction is complete, mercury or silver fulminate crystallizes out. For the manufacture of mercury fulminate on a large scale, see section on Manufacture of Commercial Products.

Mercury fulminate may also be prepared [1] by adding 1.5 grm. of oximinoacetic to 1 grm. of mercuric nitrate dissolved in 3 c.c. of nitric acid (sp. gr. 1.34) and 2 c.c. of water, and the reaction allowed to proceed without cooling; 0.1 to 0.2 gr. of mercuric fulminate is obtained.

Fulminic acid is produced by the action of dilute mineral acids on aminomethylnitrolic acid, $ONC(NH_2)$:-NOH, or on aminoformoxime, $H_2NCH : NOH$.[2]

When a solution of mercury in an excess of dilute nitric acid is treated with a strong aqueous solution of malonic acid and a few c.c. of sodium nitrite solution, carbon dioxide is evolved the temperature of the mixture rises, and crystals of the mercury fulminate may be separated on cooling.[3]

Mercury fulminate, $HgC_2N_2O_2$, crystallizes in white

[1] H. Wieland, *Ber.* (1910), **43**, 3362 ; *J.C.S.* (1911), i. 23.

[2] H. Wieland, *Ber.*, **42**, 820–2.

[3] Angelico, *Chem. Zentr.* (1901), ii. 404.

silky needles, practically insoluble in pure cold water, slightly soluble in boiling water. It detonates violently when heated to 180° C. or when the dry powder is struck, or by friction. It may, however, be handled with comparative safety if it is moistened with 30 per cent. or more of water. It is soluble in alcohol, pyridine, and in aqueous solutions of potassium cyanide or sodium thiosulphate. The double salts, $HgC_2N_2O_2KI$ and $HgC_2N_2O_2KCNS$ [1] and $HgC_2N_2O_2KCN$ [2] have been prepared.

Silver fulminate, $Ag_2C_2N_2O_2$, is very similar to the mercury salt: it crystallizes in white opaque needles practically insoluble in water; it is more readily exploded, and explodes with greater violence than the mercury salt. The compound, $AgNH_4C_2N_2O_2$, crystallizes from hot solutions in aqueous ammonia. Similar double salts may be prepared by the action of caustic alkalis or the alkaline sulphides or chlorides.

The copper salt may be prepared by boiling the mercury salt with water and metallic copper: it is obtained on cooling the liquid in green, highly explosive crystals. The zinc salt is obtained in a manner similar to the copper salt by substituting metallic zinc for the copper. It crystallizes in colourless rhombic tablets, insoluble in water, but soluble in alkalis, and it detonates violently when struck.

Free fulminic acid is prepared in ethereal solution as described above, and a double hydrogen salt of zinc may be prepared as follows: The zinc fulminate solution is treated with an excess of barium hydroxide, and then the excess of barium removed by a current of carbon dioxide. By this means a double zinc barium fulminate is obtained; by adding the calculated quantity of dilute sulphuric acid to the double salt a zinc hydrogen fulminate is obtained. By displacing the hydrogen by different bases or the barium in the original salt with different soluble sulphates a number of double salts of zinc may be prepared.

[1] Schischkow. [2] Steiner.

FULMINURIC ACID

When mercury fulminate, but not the silver salt, is heated in aqueous solutions with a metallic chloride to 100° C., a yellow deposit of oxydimercuric ammonium chloride is formed, and about one quarter of the fulminate combines with the elements of water to form ammonia and carbon dioxide, the residue being converted into fulminuric acid:[1]

$$4C:NOH + H_2O = C_3N_3H_3O_3 + CO_2 + NH_3.$$

The remaining mercury in solution is precipitated by the addition of aqueous ammonia and the liquid filtered and the filtrate evaporated. By recrystallizing the first crop of crystals, pure ammonium fulminurate is obtained.

The free acid may be prepared in solution, by first precipitating the ammonium salt solution prepared as described above, with lead acetate, and suspending in water the filtered and washed lead fulminurate through which a current of washed hydrogen sulphide is passed. It may also be prepared by decomposing the silver or barium salt with the calculated quantity of hydrochloric or sulphuric acid respectively.

Ulpiani,[2] obtained the acid by first preparing succinamidedinitroperoxide by the action of nitric acid on ethylacetoacetate and then treating this compound with strong ammonia. Fulminuric acid is obtained together with β-isofulminuramide, the amide of β-isofulminuric acid, which may be obtained by hydrolysis.

Fulminuric acid is a monobasic acid which decomposes at 145° C.[3] When heated with sulphuric acid it yields nitroacetonitrile, and in conjunction with nitric acid trinitroacetonitrile. By heating with dilute solutions of acids or alkalis it is decomposed into oxalic acid, ammonia and carbon dioxide. It reacts with

[1] *A.*, **95**, 282; Schischkoff, *A.*, **97**, 53; **101**, 213.
[2] *Gazz.* (1905), iii. 357.
[3] Steiner, *Ber.* (1872), 381.

chlorine, forming chlorofulminuric acid, $C_3H_2ClN_3O_3$, from which the salts, $AgC_3HClN_3O_3$ and $Ag_2C_3ClN_3O_3$, may be obtained, while bromine forms the similar compound, bromofulminuric acid, $C_3H_2BrN_3O_3$.[1] The constitution of this acid seems very uncertain, for while Ulpiani [2] regards it as isonitrocyanoacetamide, Nef considers it as nitrocyanoacetamide.[3]

The acid forms a characteristic deep blue precipitate with ammoniacal copper sulphate solution.

Dry hydrochloric acid passed through suspensions of the ammonium fulminurate in alcohol forms nitromelonamide, and the ammonium salt of ethyl nitromelonate [4] thus :

$$NO_2H : C(CN)\cdot CO\cdot NH_2 \rightarrow NO_2H : C(CO\cdot NH_2)_2 \rightarrow NO_2\text{-}H\cdot C(CO_2Et)_2.$$

Ammonium fulminurate, $NH_4C_3H_2N_3O_3$, forms anhydrous monoclinic crystals soluble in water, but insoluble in alcohol. It forms the double salt, $(NH_4C_3H_2N_3O_3)_22Hg(CNS)_2$. The barium salt, $Ba(C_3H_2N_3O_3)_22H_2O$, crystallizes in prisms (Liebig). The magnesium salt, $Mg(C_3H_2N_3O_3)_25H_2O$, crystallizes in needles (Steiner). The mercury salt, $Hg(C_3H_2N_3O_3)_2$, crystallizes in prisms, and forms also the basic salt, $Hg(C_3H_2N_3O_3)_2HgO$ (Steiner). The lead salt, $Pb(C_3H_2N_3O_3)_22H_2O$, forms needle crystals. The potassium salt, $KC_3H_2N_3O_3$, may be prepared by gradually adding a strong solution of potassium chloride to a boiling solution of mercury fulminate and hydrogen sulphide then passed through the solution to remove the mercury. When pure the potassium salt may be obtained in long glistening needles.

The silver salt obtained by heating the ammonium or potassium salt solution with silver nitrate is almost insoluble in cold water, but is slightly soluble in boiling water, from which it may be crystallized in long thin needles. This salt, when heated with concen-

[1] Ehrenberg, *J. pr. Chem.* [2], 33, iii.
[2] *Gazz.* (1905), iii. 357.
[3] *A.*, **280**, 329.
[4] Ulpiani, *Gazz.* (1912), **42** i 390.

trated hydrochloric acid to 110° C., one-third of the total nitrogen passes into hydroxylamine hydrochloride and the other two-thirds form ammonium chloride (Ehrenberg). The zinc salt, $Zn(C_3H_2N_3O_3)_25H_2O$, crystallizes in needles.

Several isomeric fulminuric acids are known, the constitution of which is still the subject of much controversy.

CHAPTER VII

THIOCYANATES, SELENOCYANATES

THIOCYANATES, GENERAL REACTIONS

THE alkali metal cyanides combine directly with sulphur, 1 molecule of the cyanide taking up 1 atom of sulphur, to form a class of compounds known as thiocyanates (sulphocyanides) of the general formula, M'CNS.

They may be prepared by a number of reactions thus:

1. By passing hydrocyanic acid into an alkaline polysulphide solution, a thiocyanate being formed with precipitation of sulphur:

$$K_2S_3 + 2HCN = 2KNCS + H_2S$$

and

$$K_2S_5 + 2HCN = 2KNCS + H_2S + S_2.$$

2. By heating ammonium sulphocarbonate to 100° C.:

$$(NH_4)_2CS_3 = NH_4CNS + 2H_2S.$$

3. By the action of heat on ammonia and carbon disulphide under pressure:

$$2NH_3 + CS_2 = NH_4CNS + H_2S.$$

4. By heating a solution of a ferrocyanide with a polysulphide under a pressure of 30 lb. per sq. in.:

$$K_4Fe(CN)_6 + 2K_2S_5 = 6KCNS + FeS + K_2S_3.$$

5. By boiling a solution of a cyanide with a polysulphide or with sulphur:

$$4KCN + K_2S_5 = 4KCNS + K_2S$$

and

$$KCN + S = KCNS.$$

6. By fusing a dry ferrocyanide with an alkali and sulphur.

7. And by heating a solution of a ferrocyanide and thiosulphate under 150 lb. pressure per sq. in. :

$$Na_4Fe(CN)_6 + 6Na_2S_2O_3 = 6NaCNS + 2Na_2SO_3 + 3Na_2SO_4 + FeS.$$

Thiocyanates occur to the extent of $\frac{3}{4}$ to 1 per cent. in the crude liquor from the ammonia scrubbers of a gas works, and from 0.1 to 2 per cent. or 3 per cent. in spent oxide of iron obtained from the same source. Small traces have been detected in the saliva of man.

The thiocyanates of the alkali and alkaline earth metals, and including also most of those of the heavy metals, are very soluble in water; the mercuric cadmium and cupric thiocyanates being sparingly soluble, while the lead, silver and cuprous salts are insoluble; the water soluble salts are also generally very soluble in alcohol, while the salts of iron, chromium, cobalt, etc., are soluble in ether.

The ferric salt, which is very soluble in water, alcohol and ether, is of a deep blood-red colour, and the formation of the characteristic colour of this compound by the addition of an iron salt to the solution of a thiocyanate is the test usually applied for the detection of these salts.

A large number of soluble double salts of the alkali or alkaline earth metals, with the thiocyanates of the heavy metals, are known. The double salts of iron, chromium, manganese, mercury, cobalt, nickel and zinc, etc., are generally very soluble in water and are stable on dilution, but the double salts of silver and cuprous thiocyanates are stable only in the presence of an excess of the alkali thiocyanate, the whole of the heavy metal thiocyanate being precipitated on dilution.

The thiocyanates are decomposed by oxidizing agents in acid solution, the sulphur being oxidized to sulphuric acid with liberation of hydrocyanic acid :

$$2M'CNS + 3O_2 + 2H_2O = 2MHSO_4 + 2HCN.$$

The sulphur can also be removed by fusing the dry salt with metallic iron :

$$KCNS + Fe = KCN + FeS.$$

Hydrogen bubbled through the dry fused alkali metal thiocyanate yields hydrogen sulphide and hydrocyanic acid in the form of vapour and leaves a residue of a fused mass of a mixture of cyanide and sulphide of the alkali metal. The first action of the hydrogen is the production of an alkali metal cyanide, and hydrogen sulphide, thus :

$$KCNS + H_2 = KCN + H_2S.$$

Some of this hydrogen sulphide then reacts, however, with the newly formed cyanide, forming a sulphide with evolution of hydrocyanic acid :

$$2KCN + H_2S = K_2S + 2HCN.$$

By the action of hydrogen on the fused alkaline earth thiocyanates, similar products are obtained, but a considerable proportion of the cyanogen is destroyed with formation of carbon disulphide and ammonia.

The dry thiocyanates of potassium or ammonium when intimately mixed with aluminium powder and heated to a high temperature in a covered crucible, react with formation of aluminium nitride, some aluminium sulphide being formed by a secondary reaction :

$$2KCNS + 2Al = K_2S_2 + Al_2N_2 + 2C.$$

The nitrides of boron and magnesium may be obtained in a similar manner.[1]

When reduced by nascent hydrogen in aqueous solution, methylamine and hydrogen sulphide are obtained :

$$MCNS + 3Zn + 8HCl = CH_3NH_2HCl + H_2S + MCl + 3ZnCl_2.$$

Heated to 120° C. with an excess of slaked lime, thiocyanates are decomposed, the whole of the nitrogen appearing in the form of ammonia :

$$2MCNS + 3Ca(OH)_2 = 2NH_3 + 2CaS + CaCO_3 + M_2CO_3.$$

[1] A. Vournasos, *Z. anorg. Chem* (1912), **77**, 191–6.

Nitric acid acts on a thiocyanate in aqueous solution oxidizing the sulphur to sulphuric acid with liberation of hydrocyanic acid. Concentrated hydrochloric acid added to a moderately strong aqueous solution of a thiocyanate liberates a little hydrocyanic acid with formation of a sparingly soluble yellow crystalline precipitate of perthiocyanic acid.

A dry thiocyanate heated with concentrated sulphuric acid is completely decomposed. Carbon dioxide and monoxide, together with sulphur dioxide, are given off as gases, and the sulphates of ammonium and the base of the thiocyanate are left in the residue :

$$2MCNS + 6H_2SO_4 = M_2SO_4 + (NH_4)_2SO_4 + 2CO + 2H_2O + 6SO_2.$$

A strong aqueous solution of a thiocyanate heated with sulphuric acid yields carbon oxysulphide and ammonium sulphate, thus :

$$MCNS + 2H_2SO_4 + H_2O = COS + MHSO_4 + NH_4HSO_4.$$

This reaction does not occur if the solutions are dilute, hydrothiocyanic acid only being liberated, which may be distilled off. Part of the acid, however, is decomposed in the presence of steam.

When chlorine is passed through a moderately strong solution of a thiocyanate, a yellow amorphous body is formed, known as pseudosulphocyanogen, which at one time had a limited application in the textile industry as a yellow dye, under the name of Canarine. This compound, when fused with caustic potash, yields potassium thiocyanate and cyanate.

A solution of bromine in a 10 per cent. solution of potassium bromide reacts with aqueous thiocyanates with formation of cyanogen bromide and sulphuric acid : [1]

$$KCNS + 4Br_2 + 4H_2O = KBr + CNBr + H_2SO_4 + 6HBr.$$

Acetic acid heated with a dry thiocyanate yields acetyl perthiocyanic acid.

[1] W. Konig, *J. pr. Chem.* (1911) ii. **84**, 558–62.

Many of the metallic thiocyanates combine directly with ammonia, pyridine, hexamethylenetetramine, etc., to form addition compounds.

The following compounds with hexamethylenetetramine have been described by Billows : [1] $Mg(CNS)_2X_2 \cdot 9H_2O$; $Mn(CNS)_2X_2 4H_2O$; $Co(CNS)_2X4H_2O$; $Ni(CNS)_2 X4H_2O$; $Fe(CNS)_2X4H_2O$; and by F. Calzolari,[2] $NaCNSX4H_2O$; $2KCNSX$; $2NH_4CNSX$; $Ba(CNS)_2X_2 \cdot 6H_2O$.[3] Compounds with caffeine and other organic bases have been prepared.

When a thiocyanate and benzoic acid are heated together, hydrogen sulphide, carbon dioxide and benzonitril are formed :

$$HCNS + C_6H_5COOH = C_6H_5CN + H_2S + CO_2.$$

THE METALLIC THIOCYANATES

ALUMINIUM THIOCYANATE may be prepared by double decomposition between solutions of the barium salt and aluminium sulphate. The strong solution of the salt in water is syrupy and uncrystallizable. On heating this strong solution, which boils at 114° to 115° C., decomposition occurs; sulphuretted hydrogen and hydrocyanic acid are evolved and yellow crystals of perthiocyanic acid deposited. It does not appear to form double salts crystallizable from aqueous solution.

THE AMMONIUM SALT, NH_4CNS, may be obtained by decomposing cuprous thiocyanate with ammonium sulphide, by precipitating the calcium or barium salts with ammonium carbonate, or it may be prepared synthetically.

The salt crystallizes in colourless anhydrous plates, which deliquesce on exposure to the atmosphere, and are very soluble in water and alcohol, one part of water dissolving 1.62 parts of the salt at 20° C. The

[1] *Z. Kryst. Min.* (1912), **50,** 504–9.

[2] *Atti R. Accad. Lincei* (1912), [v], **21,** i. 563–9; *J.C.S.* (1912), i. 609.

[3] X = 1 molecule of hexamethylenetetramine.

dry salt melts at 159° C., and if kept for some time at this temperature the greater part is gradually converted into thiourea :

$$NH_4CNS \rightleftarrows (NH_2)_2CS.$$

This action is similar to the polymerization of ammonium cyanate into urea.

If the temperature of the melted salt is raised to 190° C. and kept there for some time, hydrogen sulphide, carbon disulphide and ammonia are evolved and guanidine thiocyanate is left in the residue :

$$2NH_4CNS = CH_5N_3HCNS + H_2S.$$

If the temperature is increased, further changes take place; mellone and finally melam is produced with evolution of the gases mentioned above.

The salt forms a number of double salts with the thiocyanates of the heavy metals; and the dry salt when exposed to dry ammonia absorbs considerable quantities of that gas with deliquescence.[1] At 0° C. 43 per cent of NH_3 is absorbed; at 25° C., 31.16 per cent.; at 50° C., 19.4 per cent.; at 75° C., 6.17, and at 100° C., none is absorbed.

Certain soluble or freshly precipitated metallic hydroxides, when boiled with a solution of ammonium thiocyanate, drive off the whole or part of the ammonia. These reactions may be divided into four classes :[2]

1. Those in which complete decomposition occurs, *e.g.* by boiling with alkali metal or alkaline earth metal hydroxides, including lithium and magnesium hydroxide :

$$NH_4CNS + MOH = MCNS + H_2O + NH_3.$$

2. Those in which salts of complex cations are formed, *e.g.* with zinc or cupric hydroxide :

$$2NH_4CNS + Zn(OH)_2 = Zn(NH_3)_2(CNS)_2 + 2H_2O$$

and

$$2NH_4CNS + Cu(OH)_2 = Cu(NH_3)_2(CNS)_2 + 2H_2O.$$

[1] W. P. Broadley and W. B. Alexander, *J. Am. Chem. Soc.* (1912), **34**, 15–24.

[2] Herman Grossmann, *Z. anorg. Chem.* (1908), **58**, 265–71; *J.C.S.* (1908), i. 512.

3. Those in which salts of complex anions are formed, *e.g.*:

$$4NH_4CNS + Ag_2O = 2NH_4[Ag(CNS)_2] + 2NH_3 + H_2O$$

and

$$4NH_4CNS + Co(OH)_2 = (NH_4)_2[Co(CNS)_4] + 2NH_3 + 2H_2O.$$

4. Those in which salts containing both complex anions and cations are formed, *e.g.* $Hg_2ONH_2(CNS)_2$; $(NH_4)_2Hg(CNS)_4$; $Cd(NH_3)(CNS)_2$; $Cd(NH_3)_2(CNS)_2$; $(NH_4)_2Cd(CNS)_4 2H_2O$.

The compounds, $Ni(NH_3)_2(CNS)_2$, in bluish-green crystals, and $Ni(NH_3)_4(CNS)_2$, in dark blue crystals, have also been prepared. The hydroxides of iron and aluminium, chromium, glucinium, etc., having but slightly basic properties, have practically no action on ammonium thiocyanate solutions.

BARIUM THIOCYANATE, $Ba(CNS)_2 2H_2O$, which may be easily prepared by boiling the cuprous or the ammonium salt with barium hydroxide, crystallizes from water in long shining deliquescent needles containing 2 molecules of water of crystallization, and from methyl or ethyl alcohol combined with 2 molecules of the solvent. The specific gravity of the saturated solution at 15° C. is 1.705, and it contains 60.79 per cent. $Ba(CNS)_2$, or 100 c.c. of saturated solution at 15° C. contain 103.7 grm of $Ba(CNS)_2$. It loses its water of crystallization at a little above 100° C., and it forms a number of well-defined double salts with the soluble thiocyanates of the heavy metals. It also forms the crystalline salt, $Ba(CNS)_2Hg(CN)_2$, when the two salts are crystallized together. Mercuric bromide dissolves in the warm concentrated solution, and the double salt, $Ba(CNS)_2 2HgBr_2 5H_2O$, separates, on cooling, in glistening needles.

THE BERYLLIUM (GLUCINIUM) SALT is very soluble and crystallizes with difficulty.

THE BISMUTH SALT forms a yellow powder, but several double salts have been prepared by L. Vanino and O. Hauser.[1] When an excess of potassium thio-

[1] *Chem. Zeit.* (1901), **25** [92], 327; *J.S.C.I.*, **21**, 66.

cyanate is added to a solution of bismuth nitrate containing mannitol followed by 5 to 6 times its volume of alcohol, a precipitate of mannitol and potassium nitrate is formed after several hours. By evaporating the filtrate the double salt, $Bi(CNS)_3 3KCNS$, is obtained in large brick-red crystals which are stable. It dissolves readily in alcohol, but is decomposed by water and is slightly deliquescent.

By using a large excess of the potassium salt, the double compound, $Bi(CNS)_3 9KCNS$, is obtained in deep red crystals with a greenish iridescence, which, however, are very hydroscopic and decompose on standing. Similar ammonium compounds have also been prepared.

BORON THIOCYANATE has been prepared by the action of boron bromide on silver thiocyanate in the presence of benzene. On evaporating the solution the thiocyanate crystallizes out in glistening crystals, but it is very unstable.[1]

CADMIUM THIOCYANATE, $Cd(CNS)_2$, is best prepared by adding cadmium sulphate to a moderately dilute solution of the barium salt and crystallizing the filtered solution. The salt is obtained in bright, colourless, anhydrous crystals, which are sparingly soluble in water. Crystallized from a solution in ammonia, the compound, $Cd(CNS)_2 4NH_3$, separates, and the salts, $Cd(NH_3)(CNS)_2$; $Cd(NH_3)_2(CNS)_2$ and $(NH_4)_2Cd(CNS)_4 2H_2O$, are formed by boiling ammonium thiocyanate solution with cadmium hydroxide. It crystallizes with mercuric cyanide to form the compound, $Cd(CNS)_2 2Hg(CN)_2 4H_2O$, and with the haloid salts of the alkali metals[2] to form the following compounds: $Cd(CNS)_2 2KCl$; $Cd(CNS)_2 2NH_4Cl$; $Cd(CNS)_2 NH_4Br H_2O$; $Cd(CNS)_2 KBr H_2O$; $Cd(CNS)_2 2KBr$; $Cd(CNS)_2 2NH_4Br$. It also forms crystalline compounds with hexamethylenetetramine, quinine, caffeine, etc.

CAESIUM THIOCYANATE, prepared by the action

[1] H. Cocksedge, *J.C.S.*, **93**, 2177–9.

[2] H. Grossmann, *Z. anorg. Chem.* (1903), **37**, 411–47.

of the sulphate on the barium salt, is exceedingly soluble in water and alcohol. It forms the double salt, $Cs_3Fe(CNS)_6 2H_2O$, which crystallizes only from concentrated solution, and the compound, $CsCu'(CNS)_2$, which is the only representative of the true double salt of cuprous thiocyanate; and the salts, $Cs_3Ag(CNS)_4$; $Cs_2Ag(CNS)_3$; $CsAg(CNS)_2$, and $Cs_2Mg(CNS)_4 2H_2O$.[1]

CALCIUM THIOCYANATE may be prepared by boiling the cuprous or the ammonium salt with lime, and passing carbon dioxide through the solution to remove the excess of lime. The salt crystallizes with difficulty from aqueous solutions, and the crystals, which contain three equivalents of water of crystallization, are very deliquescent and very soluble. The saturated solution boils at 143° C., and has a powerful action on paper, which under its action thickens and becomes gummy in a manner similar to the action of caustic soda solution. It forms a series of double salts with the heavy metal thiocyanates, and with mercuric cyanide it forms the crystalline double salt, $Ca(CNS)_2 2Hg(CN)_2 8H_2O$.

THE CERIUM SALT, $Ce(CNS)_3 7H_2O$, which may be prepared by the action of the sulphate on the barium salt, is very soluble and decomposes a little on evaporation. Its solution is said to form the double salt, $Ce(CNS)_3 3Hg(CN)_2 12H_2O$.

CHROMIC THIOCYANATE, $Cr(CNS)_3$. Freshly precipitated chromic hydroxide dissolves readily in dilute hydrothiocyanic acid forming a reddish-violet solution of chromic thiocyanate. It can also be prepared by precipitating the barium salt with chromic sulphate. The solution so prepared decomposes on boiling, but may be evaporated to dryness over sulphuric acid or calcium chloride, whereby it yields a dark green deliquescent, amorphous mass.

A number of well-defined crystalline double salts are known. The barium salt may be best prepared by exactly precipitating half of a solution of barium thiocyanate with chromic sulphate, then adding the

[1] H. L. Wells, *J. Am. Chem. Soc.* (1902), **28**, 245–84.

remainder of the barium salt and evaporating the filtered solution. The double barium chromic thiocyanate crystallizes in reddish-violet crystals. From the barium salt the corresponding potassium, sodium, ammonium, etc., salts may be obtained, by precipitating the barium with the corresponding sulphates.

When finely powdered potassium bichromate is gradually added to fused ammonium thiocyanate, ammonia is rapidly evolved, and the fused mass becomes solid. At this stage the product is treated with hot water and filtered, solid ammonium chloride is then added to the filtrate until the liquid is saturated with the salt : on cooling, small bright red shining crystals separate, which are very soluble in ether and alcohol. These crystals consist of the ammonium salt of a complex chromammonic thiocyanate.

The potassium salt may be obtained in ruby-red crystals by boiling the ammonium salt with excess of potassium chloride and the sodium salt in a similar manner with sodium chloride.

The solution of the potassium or ammonium salt forms characteristic precipitates with the heavy metals, thus with mercuric chloride a flocculent rose-coloured precipitate is obtained, insoluble in water and in dilute acids ; with copper solution and sulphurous acid a yellow precipitate of the cuprous salt ; with silver nitrate a rose-coloured insoluble precipitate, and with lead salts a yellowish-red precipitate soluble in boiling water. Hydrogen sulphide passed through a suspension of the mercury salt in water forms a red solution of the hydrogen salt, which, however, decomposes on boiling, but may be evaporated at low temperatures.

A sparingly soluble green complex chromium salt, which contains a thiocyanogen group, has been described by R. E. Weinland and E. Büttner: [1]

$$\left[\begin{matrix}(OAc)_6\\ Cr_3(OH)_3\\ CNS\end{matrix}\right] H.2H_2O.$$

[1] *Z. anorg. Chem.* (1912), **75**, 293 ; *J.C.S.* (1912), i. 530.

It is soluble in alkalis and in alcohol : with pyridine it yields **hexa-acetato-tripyridine-trichromium thiocyanate.**

Amminohexacetatodioltrichromium thiocyanate, $[NH_3Cr_3NCS(OH)_2(OAc)_6]$, prepared from chloropentammoniochromium chloride, potassium thiocyanate and acetic acid, has been described by A. Werner.[1] It is obtained in light green needles and is precipitated from its aqueous solutions by certain metallic salts. Silver nitrate or nitric acid precipitates the compound :

$$[NH_3Cr_3H_2O(OH)_2(OAc)_6]NO_3$$

in dark green prisms, and from this compound the iodide may be obtained by sodium iodide.

Difluorotetrapyridinechromium thiocyanate, $[CrPy_4F_2]SCN$, may be obtained in violet needles, by the interaction of potassium thiocyanate and difluorotetrapyridinechromium nitrate. The latter body is prepared by the interaction of hexoaquochromium fluoride, potassium nitrate and pyridine, the mixture being heated on the water-bath for some time until the solution lightens in colour.

COBALT THIOCYANATE, $Co(CNS)_2 3H_2O$, may be obtained by dissolving the carbonate or hydroxide in hydrothiocyanic acid, but is conveniently prepared by double decomposition of the solution of the sulphate and barium thiocyanate. The solution, which is of a red colour when dilute, changes to a deep indigo blue when heated or concentrated. The salt crystallizes in well-formed crystals of the above composition, and of a deep red colour, which in the larger crystals appears almost black. When heated to 100° C. the crystals become anhydrous, but both the anhydrous and the hydrated form absorb moisture from the air and deliquesce.

The addition of mercuric chloride to a strong solu-

[1] *Ber.*, **41**, 3447–64.

[2] N. Costachescu, *Ann. Sci. Univ. Jassy* (1912), **7**, 87–100 ; *J.C.S.* (1912), i. 493.

tion of the thiocyanate changes the blue colour to pink, and the compound, $2Co(CNS)_2 3HgCl_2$, may be obtained in pink crystals. Zinc chloride also produces the same colour change.[1]

Cobaltous thiocyanate forms a large number of double salts with the soluble thiocyanates of the other metals. These may be prepared by dissolving equivalent quantities of the two salts in water and crystallizing, but they are more readily obtained by precipitating the barium salt with the corresponding metallic sulphate. Barium cobaltous thiocyanate is prepared by dissolving 116 grm. of barium thiocyanate in 500 c.c. of distilled water: 250 c.c. of this solution are then exactly precipitated by 56 grm. cobaltous sulphate; the resulting solution is then mixed with the remaining 250 c.c. of barium thiocyanate solution, the whole filtered from the barium sulphate and the filtrate evaporated.

Deep purple-blue crystals are obtained of the composition, $BaCo(CNS)_4 7H_2O$, which become anhydrous when heated to 100° C. and are non-deliquescent, this latter property being a general one for these double salts. By precipitating a solution of this salt with the corresponding sulphates the following double salts may be prepared. The ammonium cobaltous salt, $(NH_4)_2Co(CNS)_4 3H_2O$, small purple-blue needles; the cadmium salt, $CdCo(CNS)_4$, crystallizes in dark blue, sparingly soluble anhydrous crystals. The lithium salt, $Li_2Co(CNS)_4 8H_2O$, crystallizes in dark blue needles which are very soluble in alcohol, and are deliquescent. The magnesium salt, $MgCo(CNS)_4 8H_2O$, loses 50 per cent. of its water of crystallization at 100° C., and the crystals then fuse and turn brown, but on exposure to the air the 4 molecules of water are reabsorbed, the colour again changing to blue. The potassium salt, $K_2Co(CNS)_4 3H_2O$, is very soluble in water and alcohol, and is also soluble in many organic liquids such as alcohols, aldehydes, ketons, acids and nitrobenzol, but not in mineral oils

[1] A. Hantzsch and Shitaba, *Z. anorg. Chem.* (1912), **73**, 309.

or hydrocarbons.[1] At 100° C. the salt has the composition, $[K_2Co(CNS)_4]_2H_2O$. The sodium salt, $Na_2Co(CNS)_4 7H_2O$, forms very soluble non-deliquescent crystals which lose 5 molecules of water at 100° C., the colour changing to brown. On exposure to the air the water is reabsorbed, the blue colour returning. The zinc salt, $ZnCo(CNS)_4 7H_2O$, crystallizes in deep blue crystals, but of somewhat lighter shade than the majority of these salts.

The calcium and the strontium double salts, $SrCo(CNS)_4 8H_2O$, may be prepared by crystallizing equivalent quantities of the two thiocyanates. They are more soluble than the preceding salts and crystallize with greater difficulty.

The addition of a mercuric salt to a solution of cobalt thiocyanate, or of any soluble thiocyanate to a solution containing both cobalt and mercury salts, yields a precipitate of the deep blue double mercuric cobaltous thiocyanate, which is sparingly soluble in water.

The salts, $Cs_2Co(CNS)_4 2H_2O$ and $CoAg(CNS)_3 2H_2O$, as brilliant deep blue crystals, which turn dark green when anhydrous and the triple salt, $Cs_2CoAg_2(CNS)_6 2H_2O$, in bright pink crystals have been prepared by Wells and his co-workers.[2]

By the action of ammonia on cobalt thiocyanate, J. Sands [3] prepared the compound cobalto tetrammonic thiocyanate, $Co(CNS)_2(NH_3)_4$, in rose-red needles. The oxidation compound, $O_2[Co(NH_3)_5(CNS)_2]_2$, was formed as a by-product. The double salt, $(NH_4)_2Co(CNS)_4 3H_2O$, may also be prepared by boiling ammonium thiocyanate solution with cobaltous hydroxide.

Many double salts with organic compounds have been prepared and described; thus the compound, $Co(CNS)_2 2C_6H_{12}N_4HCNS$, may be prepared by adding hexamethylenetetramine thiocyanate to a solution of

[1] Jan von Zawidski, *J.C.S.* (1910), A ii. 562.
[2] *J. Am. Chem. Soc.* (1903), **29**, 474–8.
[3] *Ber.* (1903), **36**, 1436–7.

cobaltous thiocyanate in excess of strong aqueous ammonia. This salt, unlike the metallic double salts, which are blue, separates in lilac-coloured crystals.[1]

Additive compounds with hexamethylenetetramine are also known; the compound, $Co(CNS)_2 2C_6H_{12}N_4 \cdot 4H_2O$, crystallizes in rose-coloured scales, which lose 1 molecule of hexamethylenetetramine on recrystallization, and the compound, $Co(CNS)_2C_6H_{12}N_4 \cdot 4H_2O$, is obtained in dark red tabular crystals.[2]

Tetrapyridine cobaltous thiocyanate, $Co(CNS)_2 4C_5H_5N$, is obtained by dissolving cobaltous chloride in alcohol, and shaking with potassium thiocyanate and pyridine. It forms a peach-coloured precipitate, which dissolves in ammonia with a yellow colour, and gives an ultramarine blue when treated with dilute sulphuric or hydrochloric acid.[3]

When the pyridine compound is treated with iodine in a boiling alcoholic solution, the salt, $[CoPy_4(CNS)_2]2I_2$, separates on cooling, in black lustrous crystals, which when heated to 100° C. lose all the iodine and half the pyridine.[4]

CUPRIC THIOCYANATE, $Cu(CNS)_2$, is formed as a black precipitate when a solution of a thiocyanate is added to a moderately strong solution of a copper salt. It is, however, decomposed rapidly into the cuprous salt by washing, or by dilution with water. If filtered and gently dried without washing it can be kept for some months consisting mainly of the cupric salt, but it gradually passes into the cuprous compound. The black precipitate dissolves readily in ammonia solution, forming a deep blue liquid, which on evaporation yields fine blue needles of the composi-

[1] J. Calzolari, *Ber.* (1910), **43**, 2217, 2219.

[2] G. A. Barbieri and F. Calzolari, *Atti R. Accad. Lincei* (1911), v. 26, i. 119–5; *J.C.S.* (1911), i. 267.

[3] F. Reitzenstein, *Z. anorg. Chem.* (1902), **32**, 298; *J.C.S.* (1903), 1, iii.

[4] P. Pfeiffer and M. Tilgner, *Z. anorg. Chem.* (1908), **58**, 433; *J.C.S.* (1908), 1, 614.

tion, $Cu(CNS)_2 4NH_3H_2O$, which are stable in the air.

Compounds with pyridine and hexamethylenetetramine have been prepared by J. Calzolari.[1] A concentrated solution of cupric nitrate is added to a saturated solution of ammonium thiocyanate until the black precipitate which at first forms redissolves. It is then filtered and a concentrated solution of pyridine thiocyanate added, and the salt tripyridinium cupric thiocyanate obtained as a reddish-brown precipitate. By substituting hexamethylenetetramine thiocyanate for the pyridine salt, dihexamethylenetetramine cupric thiocyanate, $Cu(CNS)_2 2C_6H_{12}N_4HCNS$, may be prepared as a light green crystalline precipitate.

CUPROUS THIOCYANATE, CuCNS, is precipitated when a solution of a soluble thiocyanate is treated with a cupric salt in the presence of a reducing agent, such as sulphurous acid or ferrous sulphate, as a very finely divided white, amorphous precipitate. It is anhydrous and stable in the air, and is insoluble in water or alcohol, but dissolves in aqueous ammonia from the solution of which it can be made to crystallize combined with ammonia. When this compound is exposed to the air, however, all the combined ammonia is liberated.

Cuprous thiocyanate is readily decomposed by the alkaline hydroxides, and is easily soluble in a concentrated solution of a soluble thiocyanate and the thoroughly saturated solution when concentrated will yield crystals of a double cuprous thiocyanate.

The double salt, 6KCNSCuCNS, has been described by Thurnauer,[2] and the salt, $CsCu(CNS)_2$ by H. Wells;[3] this salt is the only true double salt of cuprous thiocyanate yet prepared. The salt, $Na_3Cu(CNS)_4 4H_2O$, has been prepared by the author. A strong solution of this salt acts very rapidly on pure filter paper, causing

[1] *Ber.* **43**, 2217; *J.C.S.* (1910), i. 614.
[2] *Ber.* (1890), **23**, 776.
[3] *J. Am. Chem. Soc.* (1902), **28**, 245.

it to swell and thicken, and if the mixture is warmed the paper dissolves to a clear solution, which sets to a jelly on cooling. The barium salt has the composition $Ba_3Cu'(CNS)_7{}_{10}H_2O$.

All these double salts are completely decomposed when dissolved in water, the whole of the cuprous thiocyanate being precipitated, but this precipitate redissolves when the liquor becomes concentrated.

GOLD THIOCYANATES. The auric salt is obtained as a reddish coloured precipitate when an excess of auric chloride is added to a soluble thiocyanate. This precipitate is soluble in ammonia, and in excess of the thiocyanate solution.

When the auric chloride solution is added to an excess of potassium thiocyanate solution, the double salt potassium auric thiocyanate, $KAu(CNS)_4$, separates as a bulky orange red precipitate, which redissolves on boiling with formation of potassium aurous thiocyanate.

The double aurous compound is best prepared by adding a neutral solution of auric chloride to a solution of potassium thiocyanate heated to 80° C. On evaporation the liquor yields the salt as yellow prisms.

HYDROTHIOCYANIC ACID, HCNS, may be prepared in aqueous solution by adding the calculated quantity of sulphuric acid to a solution of the barium salt, or by passing hydrogen sulphide through the lead or mercury salt suspended in water or the solution of the zinc, nickel, etc., salts.

The anhydrous acid may be obtained by passing carefully dried hydrogen sulphide over the dry mercury salt.[1] It can, however, be obtained in a state of greater purity by the method of A. Rosenheim and R. Levy,[2] who prepare it thus: Concentrated sulphuric acid is allowed to drop slowly on to a mixture of potassium thiocyanate and phosphoric acid in an atmosphere of hydrogen and at a pressure of 40 to 60 m.m. The pure hydrothiocyanic acid which is

[1] Hermes, *J. pr. Chem.*, **97**, 465.

[2] *Ber.* (1907), **40**, 2166–9.

evolved can be condensed in a cooled receiver in the form of white crystals which melt at 5° C.

By substituting potassium bisulphate for the sulphuric acid in the method described above, W. Rück and H. Steinmetz state [1] that increased yields may be obtained, the acid also being free from colour.

The anhydrous acid has a corrosive action on the skin. It dissolves in water at 0° C. without decomposition, but at higher temperatures it changes rapidly to a yellow polymeride: the aqueous solution also decomposes, especially when heated, into carbon dioxide, carbon disulphide, ammonia and hydrogen sulphide thus:

$$2HCNS + 2H_2O = CO_2 + CS_2 + 2NH_3$$

and

$$HCNS + 2H_2O = CO_2 + H_2S + NH_3.$$

The strong aqueous acid is decomposed by heat into hydrocyanic and perthiocyanic acids, but when boiled with mineral acids it yields carbon dioxide ammonia, hydrogen sulphide, or carbon oxysulphide according to the strength of the acid.

HEXAMETHYLENETETRAMINE THIOCYANATE is prepared by adding hydrochloric acid to a solution of hexamethylenetetramine (1 molecule) and ammonium thiocyanate (1 molecule), in the form of a saturated solution. The salt crystallizes out in large transparent monoclinic prisms.[2]

FERRIC THIOCYANATE, $Fe(CNS)_3 1\frac{1}{2}H_2O$, is obtained as a pure aqueous solution by the general method with ferric sulphate and the barium salt, or as an ethereal solution by shaking an aqueous solution of any soluble thiocyanate mixed with a ferric salt, with ether. The salt forms very dark red, nearly black, deliquescent crystals, which are very soluble in water, alcohol, and ether. Its solubility in ether is such that it may be completely extracted from its aqueous solutions by shaking with ether.

[1] *Z. anorg. Chem.* (1912), **77**, 51–89.

[2] J. Calzolari, *Ber.* (1910), **43** 2217–9.

The aqueous solution slowly decomposes on boiling, hydrothiocyanic acid and its decomposition products are evolved, and the ferric thiocyanate reduced to the ferrous salt; this reduction has been shown by J. C. Philips and A. Bramley [1] to be at the expense of the thiocyanate, which, however, forms carbon dioxide, ammonia and sulphuric acid and not hydrocyanic acid thus:

$$8Fe(CNS)_3 + 6H_2O = 8Fe(CNS)_2 + 7HCNS + CO_2 + H_2SO_4 + NH_3.$$

The red colour of the ferric thiocyanate is always produced when a neutral or acid solution of a ferric salt is added to a soluble thiocyanate, but is destroyed by the addition of phosphoric arsenic, iodic and oxalic acids, and by mercuric chloride and also by considerable dilution, but in the latter case it is restored by the addition of hydrochloric acid. The test, however, does not answer when a basic ferric salt solution is used.[2]

Ferric thiocyanate forms a series of double salts with other metallic thiocyanates, and it also yields crystalline compounds with certain organic bases, which contain 3 molecules of the base for each molecule of the thiocyanate.[3]

Tripyridine ferric thiocyanate, $Fe(CNS)_3(C_5H_5N)_3$, may be prepared by mixing the calculated quantity of ferric thiocyanate and pyridine in aqueous, or better still in ethereal solution: it forms dark green crystals which are insoluble in water, but soluble in many organic solvents, forming a red or violet solution.

Triquinoline ferric thiocyanate, $Fe(CNS)_3(C_9H_7N)_3$, prepared in a similar manner to the pyridine compound described above, forms almost black crystals, while the triantipyrine ferric thiocyanate, $Fe(CNS)_3(C_{11}H_{12}ON_2)_3$, yields red crystals.

The potassium double salts, $Fe(CNS)_3 9KCNS 4H_2O$

[1] *T.C.S.* (1913), 795.

[2] H. Schulze, *Chem. Zeit.* (1893), **17**, 2; *J.S.C.I.*, **12**, 949.

[3] G. A. Barbieri and G. Pampanini, *Atti R. Accad. Lincei* (1910), [v], **19**, ii. 591.

and $Fe(CNS)_3 3KCNS$, have been prepared by Krass and Moralit.[1]

The ferrous salt, $Fe(CNS)_2 1\frac{1}{2}H_2O$, prepared by the general method from the barium salt, forms pale green crystals which are unstable. It forms double salts such as the mercury compound, $FeHg(CNS)_4$, and combines with hexamethylenetetramine to form the compound, $Fe(CNS)_2 2C_6H_{12}N_4.4H_2O$, which crystallizes in colourless scales, but which loses 1 molecule of hexamethylenetetramine on recrystallization.

LEAD THIOCYANATE, $Pb(CNS)_2$, is slowly deposited in white sparingly soluble dense crystals which are anhydrous when a neutral solution of lead acetate is added to a moderately strong solution of a thiocyanate. On boiling the crystals with water they are converted into a basic salt of the composition, $Pb(CNS)_2Pb(OH)_2$, which may also be obtained by adding a basic lead acetate solution to a thiocyanate as a white curdy precipitate.

The double salts, $Pb(CNS)_2PbBr_2$; $Pb(CNS)_2 8Pb Br_2$ and $3Pb(CNS)_2PbI_2$, and the double thiocyanate, $PbK(CNS)_3$, have been prepared by H. Wells.[2]

THE LITHIUM SALT, $LiCNS 2H_2O$, is an exceedingly soluble and very deliquescent salt, which crystallizes with difficulty in colourless crystals. It forms a number of double salts with the heavy metal thiocyanates.

MAGNESIUM THIOCYANATE, $Mg(CNS)_2 4H_2O$, forms very soluble colourless crystals which crystallize easily. A saturated solution at 15.5° C. has a specific gravity of 1.289, and contains 55.26 grm. of $Mg(CNS)_2$ per 100 c.c. It forms a large number of double salts with the metallic thiocyanates such as $MgCo(CNS)_4 8H_2O$; $MgZn(CNS)_4 9H_2O$ (H. E. W.), and $MgCs_2(CNS)_4 2H_2O$.[3] It also forms the crystalline double salt, $Mg(CNS)_2 2Hg(CN)_2 4H_2O$, when crystallized with mercuric cyanide, and with hexamethylenetetramine,

[1] *Ber.* **22**, 2061.
[2] *J. Am. Chem. Soc.* (1902), **28**, 245.
[3] Wells, *l.c.*

the compound, $Mg(CNS)_2 2C_6H_{12}N_4 10H_2O$, is obtained in colourless tablets (Calzolari).

MANGANESE THIOCYANATE, $Mn(CNS)_2 4H_2O$, forms clear, colourless, non-deliquescent crystals, which effloresce when exposed to the air. The compound is very soluble in water and alcohol, and forms a series of double salts characterized by great solubility in water. The sodium salt, $Na_2Mn(CNS)_4 6H_2O$, forms white deliquescent crystals which lose 4 molecules of water at 100° C. The barium salt is obtained in very soluble crystals, and the potassium and ammonium salt are practically uncrystallizable from aqueous solutions.

The hexamethylenetetramine compound, $Mn(CNS)_2 2C_6H_{12}N_4 4H_2O$, has been obtained in colourless tablets which can be crystallized from water unchanged.

MERCURIC THIOCYANATE, $Hg(CNS)_2$, is precipitated in small crystals when a moderately strong solution of an alkali metal thiocyanate is precipitated with an excess of mercuric chloride; or by digesting a solution of barium thiocyanate with the calculated quantity of mercuric sulphate at 100° C. until the barium is all precipitated as sulphate, filtering the boiling solution—which should be moderately dilute—and cooling the filtrate. Mercury thiocyanate crystallizes in anhydrous white needles very sparingly soluble in cold, but more soluble in hot water, and moderately soluble in alcohol. The dry salt when heated decomposes, and swells up to a bulk very many times the original volume of the salt: this property is made use of in the preparation of the toy called "Pharaoh's Serpents," of which it is the main ingredient.

The salt combines with pyridine, forming the additive compound, $Hg(CNS)_2 C_5H_5N$, in colourless monoclinic crystals:[1] it also dissolves in a hot concentrated solution of potassium or ammonium chloride which on cooling deposits the double salts, $Hg(CNS)_2 KCl$ and $Hg(CNS)_2 NH_4Cl$, respectively. In a similar manner the compounds, $Hg(CNS)_2 2KBr$ and $Hg(CNS)_2 2NH_4Br$,

[1] Grossmann and Hurseler.

may be prepared. These compounds are decomposed by water.

A well-defined and characteristic series of double mercuric thiocyanates are known. The barium salt may be prepared by digesting at 100° C. a solution of barium thiocyanate with half the theoretical quantity of mercuric sulphate necessary to precipitate the barium. When the reaction is complete the solution is filtered, and the filtrate evaporated to obtain the double salt. It crystallizes in very soluble and very dense anhydrous crystals : from the barium salt many of the other double thiocyanates may be obtained, and the following salts have been described : $Hg(NH_4)_2(CNS)_4$, very soluble, and $CdHg(CNS)_4$, which separates from water in tetragonal plates (Grossmann) ; $CoHg(CNS)_4$, in sparingly soluble deep blue crystals. This compound is formed whenever the two metals and a thiocyanate occur together in a neutral aqueous solution ; $K_2Hg(CNS)_4$, $Na_2Hg(CNS)_4$ are both very soluble salts ; $NiHg(CNS)_4 2H_2O$ separates in small sky-blue needles, and the double zinc salt which is produced whenever the two metals and a thiocyanate are present together in solution separates as a white bulky precipitate very slightly soluble in water ; 100 parts of water at 15.5°C. dissolve 0.00993 parts $ZnHg(CNS)_4$, and might almost be used as an analytical method for the estimation of either metal.

Mercurous thiocyanate is very unstable, the white precipitate first formed on adding a thiocyanate to a mercurous salt solution rapidly decomposes into mercuric thiocyanate and metallic mercury. In concentrated solutions the decomposition is almost instantaneous.

MOLYBDENUM THIOCYANATE is probably produced when a soluble thiocyanate is added to a molybdenum salt. It may be separated from the aqueous solution, like the iron compound, by shaking with ether, in which solvent it dissolves with a fine deep red colour. The solution is also decolorized by the same substances that decolorize the ferric salt.

A series of complex double salts are known, the composition and constitution of which is still the subject of controversy,[1] the formula $Mo'''(SCN)_6R_3$ being given to these salts by Rosenheim and Garfunkel, and $Mo'''(SCN)_6H_2OR_3$ by J. Maas and Sand. These salts are isomorphous with the corresponding chromium salts.

NICKEL THIOCYANATE forms an apple-green solution, which on concentration at 100° C. deposits the salt as a black crystalline powder, but when the solution is evaporated over calcium chloride a light yellow powder is obtained, $Ni(CNS)_2 1\frac{1}{2}H_2O$.

The thiocyanate dissolved in aqueous ammonia deposits dark blue crystals of the composition, $Ni(CNS)_2 4NH_3$, which lose 2 molecules of ammonia at 100° C.

Double salts which crystallize well in bluish-green crystals have been obtained.[2] Thus the ammonium salt, $Ni(NH_4)_5(CNS)_7$; the potassium salt, $NiK_5(CNS)_7 3H_2O$, and the sodium salt, $NiNa_5(CNS)_7 14H_2O$. With hexamethylenetetramine the compound, $Ni(CNS)_2 2C_6H_{12}N_4 4H_2O$, is obtained as a green crystalline powder, which on recrystallization loses 1 molecule of the base and yields emerald green tabular crystals (Barbieri and Calzolari). The tetrapyridine compound, $NiPy_4(CNS)_2$, is also known, which if boiled with iodine in alcoholic solution is converted into the compound, $(NiPy_4(CNS))_2 2I_2$, which separates in black lustrous crystals (Pfeiffer and Tilgner).

PLATINUM THIOCYANATE has not yet been isolated in a simple form, but two series of complex double salts are known.

When potassium chloroplatinate or platinic chloride is added to an equal weight of potassium thiocyanate, and the solution heated to 80° C. but not boiled, potassium platinothiocyanate, $K_2Pt(CNS)_6 2H_2O$, is formed, which separates out of the solution on cooling in fine deep red prisms, very soluble in hot water and in alcohol.

[1] J. Maas and J. Sand, *Ber.*, 41, 3367–76, 2642–6. [2] H. E. W.

The ammonium salt, $(NH_4)_2Pt(CNS)_6$, may be prepared by double decomposition of the potassium salt and ammonium sulphate, alcohol being added to precipitate the sulphates. The salt separates from the filtrate in fine red crystals. The barium salt may be produced by double decomposition between the potassium salt and barium chloride. The sodium salt, $Na_2Pt(CNS)_6 2H_2O$, is prepared as the potassium salt by substituting sodium thiocyanate for the potassium salt.

A solution of a soluble platinothiocyanate gives a grey precipitate with a copper salt, soluble in ammonia; a black crystalline precipitate with ferrous salts; a yellow precipitate with a mercurous salt, and an orange insoluble silver salt which also forms the double salt, $Ag_2Pt(CNS)_6 2KCNS$. The lead salt is soluble in water and from strong solutions golden yellow plates of the compound are obtained, which is decomposed by hot water, forming the basic salt, $PbPt(CNS)_6PbO$.

The soluble platinothiocyanates are isomorphous with the corresponding platinoselenocyanates.[1]

POTASSIUM THIOCYANATE, KCNS, crystallizes from water in anhydrous colourless crystals. It is very soluble in water, and the saturated solution at 15.5° C. has a specific gravity of 1.428, 100 c.c. of which at 15.5° C. will contain 98.97 parts of the salt. The crystals are very deliquescent and soluble in alcohol and many organic liquids. It fuses easily and may be heated to a red heat out of air contact without decomposition.

Heated in alcoholic solution with thiocarbamide, combination takes place and the double compound, $(CSN_2H_4)_3KCNS$, separates on cooling in thin lustrous needles which melt at 143° C.[2]

The concentrated solution of potassium thiocyanate dissolves the insoluble precipitates of silver cyanide, chloride and thiocyanate, and also cuprous thiocyanate, and forms with the two latter definite double

[1] E. Billows, *Z. Kryst. Min.* (1912), **50**, 509.

[2] W. Atkins and E. Werner, *T.C.S.* (1912), 1167.

thiocyanates, but from any of these solutions the insoluble compound is wholly precipitated on dilution.

The double salts, $KCNSHgBr_2$ and $2KCNSHgI_2$, have been prepared as well as a large number of double potassium thiocyanates.

SILVER THIOCYANATE, AgCNS, is precipitated as a white curdy insoluble precipitate when a silver salt in excess is added to a soluble thiocyanate. The compound is soluble in an aqueous solution of ammonia on boiling, from which it separates on cooling in beautiful sparkling plates combined with ammonia, but when washed and dried the whole of the ammonia is given off. The dry salt turns a reddish colour on exposure to light, and when treated with dry chlorine gas, free from hydrochloric acid, it is converted into silver chloride, with formation of sulphur chloride, and solid cyanogen chloride.

The salt dissolves readily in the strong solutions of the soluble thiocyanates, forming a series of double salts which may be obtained in crystals. The solutions of these double salts are completely decomposed on great dilution, the whole of the silver thiocyanate being precipitated. On concentrating the solution practically the whole of the silver thiocyanate can be made to crystallize out as a double salt, the mother liquor being left almost free from the silver salt.

A number of these double salts have been prepared by Wells:[1] $Cs_3Ag(CNS)_4.Cs_2Ag(CNS)_3$; $CsAg(CNS)_2$; $K_3Ag(CNS)_4$; $K_2Ag(CNS)_3$; $KAg(CNS)_2$, and $M''Ag_2(CNS)_4 2H_2O$, where $M'' =$ barium, strontium or calcium. The compound, $NaAg(CNS)_2H_2O$, has also been prepared.[2]

Iodine acts on silver thiocyanate to produce hydrothiocyanic acid, part of which, however, is oxidized:

$$14AgCNS + 7I_2 + 10H_2O = 14AgI + 12HCNS + 2H_2SO_4 + NH_3 + CO_2 + HCN.[3]$$

[1] *J. Am. Chem. Soc.* (1902), **28**, 245.
[2] H. E. W.
[3] Normand and Cumming, *T.C.S.* (1912), 1862.

SODIUM THIOCYANATE, $NaCNS2H_2O$, crystallizes in rhombic tables which are very soluble in water and alcohol and are very deliquescent. When heated to 100° C. the salt becomes anhydrous.

STRONTIUM THIOCYANATE, $Sr(CNS)_23H_2O$, is very deliquescent and very soluble in water and alcohol. It may be easily prepared by boiling a solution of the ammonium salt with strontium hydroxide as long as ammonia is given off: carbon dioxide is then passed through the liquid to remove the excess of the hydroxide, and the filtered solution evaporated.

THALLIOUS THIOCYANATE, TlCNS, is prepared by precipitating potassium thiocyanate with a solution of a thallium salt. The compound separates in small shining prisms very slightly soluble in cold, but more soluble in hot water, but is insoluble in alcohol or ether.

Some double salts have been prepared.

VANADIUM THIOCYANATE is obtained by treating barium thiocyanate with vanadium sulphate as a green solution, although there is some doubt as to whether this is the true colour of vanadium thiocyanate, for the double salts are violet. Bongiovanni [1] explains the green colour as the result of hydrolysis due to the presence of sulphate. Vanadium chloride and thiocyanic acid give an intense reddish-violet coloration which becomes green on addition of sulphate, or of acetate or oxalate of ammonia.

Vanadium thiocyanate forms double vanadithiocyanates of the alkali metals.

ZINC THIOCYANATE separates from its aqueous solution in anhydrous crystals which are very soluble in water and alcohol. 100 parts of water at 15.5° C. dissolve 59.9 parts of $Zn(CNS)_2$, and the resulting solution has a specific gravity of 1.343.

The salt dissolves in aqueous ammonia, and from the solution the compound, $Zn(CNS)_22NH_3$, may be obtained in crystals. The same compound may also be obtained by boiling a solution of ammonium thio-

[1] *Boll. chim. farm.* (1910), **49**, 467.

cyanate with zinc hydroxide so long as it dissolves. The compound is stable at 100° C., but is decomposed by water, with separation of zinc oxide.

The double thiocyanate of zinc and barium which may be prepared by the general method for these double salts is obtained in colourless crystals of the composition $BaZn(CNS)_4 7H_2O$; 3 molecules of water are driven off at 100° C. From the barium salt other double zinc thiocyanates may be prepared by double decomposition with the sulphates of other metals.[1] The ammonium salt, $(NH_4)_2Zn(CNS)_4 3H_2O$, crystallizes in white soluble crystals; the cobalt salt, $CoZn(CNS)_4 7H_2O$, in blue needles; the lithium salt, $Li_2Zn(CNS)_4 7H_2O$, in very soluble colourless crystals; the magnesium salt, $MgZn(CNS)_4 9H_2O$, crystallizes well in colourless crystals, which melt at 100° C. and lose 6 equivalents of water; the potassium salt, $K_2Zn(CNS)_4 3H_2O$, becomes anhydrous at 100° C., and the sodium salt, $Na_2Zn(CNS)_4 8H_2O$, is non-deliquescent.

Thiocyanate of zinc also forms the hexamethylenetetramine compound, $Zn(CNS)_2 2C_6H_{12}N_4 4H_2O$, which loses 1 molecule of hexamethylenetetramine on recrystallization.

DITHIOCYANIC ACID, $H_2C_2N_2S_2$. When moderately strong sulphuric or hydrochloric acid is added to a strong aqueous solution of a thiocyanate, some hydrocyanic acid is liberated, and a yellow, sparingly soluble, bulky but crystalline precipitate is produced of variable composition, but consisting mainly of crude dithiocyanic acid. The crystals are separated from the mother liquor by filtration on a vacuum filter, washed with a little cold water, and they may be recrystallized from hot water. The compound is sparingly soluble in water, but soluble in alcohol, and when its solution is repeatedly boiled some thiocyanic acid is gradually formed.

The potassium salt may be obtained by digesting the acid in a hot solution of alcoholic potash, in yellow

[1] H. E. W.

monoclinic crystals insoluble in alcohol, but very soluble in water. The salt when boiled in aqueous solutions is quickly converted into normal potassium thiocyanate.[1] The barium salt crystallizes in short prisms; the copper salt is obtained as a red-brown precipitate, and the lead salt as a yellow precipitate. The pure hydrogen salt may be obtained by decomposing the potassium or barium salts with sulphuric acid.

TRITHIOCYANIC ACID is known, but only in the form of its alkyl esters.[2]

SELENOCYANIDES. The element silenium, like sulphur, is capable of combining directly with the cyanogen radicle of a simple cyanide to form a series of salts.

The potassium salt may be prepared by dissolving red selenium in potassium cyanide solution, or by fusing the selenium with three times its weight of anhydrous potassium ferrocyanides. The fused mass is dissolved in absolute alcohol, carbon dioxide passed through in excess to destroy any free cyanide, and the solution filtered from the deposited crystals of potassium hydrogen carbonate. The alcohol is then distilled off, the residue dissolved in water, filtered and crystallized in a vacuum over sulphuric acid. In this process, however, most of the selenium is consumed by combination with the iron, to form iron selenide. A more economical method has been proposed by W. Muthmann and E. Schroder,[3] whereby a yield of 96 to 98 per cent. of the theoretical is said to be obtained.

Take 70 grm. of pure potassium cyanide and grind to a fine powder, and mix with 79 grm. of commercial selenium, also finely ground; place the whole in a crucible and heat until the mixture is just fused.

The melted mass, which should be of a reddish-grey colour, is treated with 40 c.c. of water and warmed on the water-bath for three to four hours, water being added from time to time to make up that lost by evaporation.

When all is in solution, the liquid is evaporated

[1] Fleischer, *A.*, **179**, 204. [2] Hofmann, *Ber.*, **13**, 1349.
[3] *Ber.* (1900), **33** [ii], 1765–9; *J.S.C.I.*, **19**, 683.

down as far as possible, and then dissolved in a litre of alcohol; carbon dioxide is passed through to decompose unaltered cyanide, and then filtered from the precipitated potassium hydrogen carbonate. The alcohol is then distilled off the filtrate, and the residue cooled, when crystals of potassium selenocyanate separate.

The acid, which is known only in solution, may be prepared by passing hydrogen sulphide through a suspension of the lead salt in water and filtering from the lead sulphide. The filtrate must be heated nearly to boiling to drive off the excess of hydrogen sulphide and the solution again filtered.

HYDROSELENOCYANIC ACID, HSeCN, has marked acid properties; it is very unstable, and is decomposed by boiling and by acids, hydrocyanic acid being liberated, with precipitation of selenium. The acid attacks iron and zinc with evolution of hydrogen.[1]

The selenocyanates of the alkali and alkaline earth metals are soluble in water, as also are many of the salts of the heavy metals, but are much less stable than the corresponding thiocyanates.

The ammonium salt, NH_4CNSe, prepared from the acid by neutralizing with ammonia, is obtained in small deliquescent needles,[2] and the barium, calcium, strontium, sodium and magnesium salts may be prepared in a similar manner. The cupric salt is first formed as a brown precipitate, which soon decomposes into hydroselenocyanic acid and copper selenide: the cuprous salt is white and insoluble. When an alcoholic solution of the potassium salt is added to a solution of gold chloride, some selenium is precipitated, but dark red crystals of the double salt, $AuK(SeCN)_2$, may be obtained by evaporating the filtrate.[3] The addition of a ferric salt to a solution of a selenocyanate produces a red coloration which rapidly decomposes.

The lead salt may be obtained by precipitation with lead acetate and recrystallizing the salt from boiling

[1] Crookes, *C.J.*, 4, 12. [2] Crookes, *l.c.*
[3] Clark, *Ber.* 11, 1326.

water in long yellow needles. Two mercury salts have been described by Cameron and Davy,[1] mercuric selenocyanate, a greyish precipitate, by adding mercuric acetate to the potassium salt, which forms the compound, $Hg(SeCN)_2HgCl_2$, with mercuric chloride, and the mercurous salt which is obtained as an amorphous precipitate.

The normal platinum salt has not been isolated, but when platinic chloride is added to potassium selenocyanate, a complex salt potassium platinoselenocyanate, $K_2Pt(SeCN)_6 2H_2O$, is formed. The corresponding ammonium salt has also been described.[2] The potassium salt prepared as above described crystallizes in white deliquescent needles; it is decomposed by acids with liberation of hydrocyanic acid and precipitation of selenium, and reacts with chlorine, forming cyanogen chloride and selenium.[3]

Several double compounds of the selenocyanates with mercury salts have been described by Cameron and Davy,[4] thus: $KCNSeHg(CN)_2$; $KCNSeHgBr_2$; $KCNSeHgI_2$; $KCNSeHgCl_2$; $KCNSeHg(CNS)_2$.

The silver salt is insoluble in water and may be obtained by precipitation. It dissolves in warm ammonia, from which it may be obtained in shining crystals, which blacken in light.

The zinc salt, $Zn(CNSe)_2$, forms non-deliquescent crystals.

[1] *T. Irish Acad.*, **27**, 145.
[2] *J.C.S.* (1912), i. 422.
[3] Kypke and Meyer, *A.*, **115**, 207.
[4] *T. Irish Acad.*, **27**, 151.

PART II

MANUFACTURE AND APPLICATION OF CYANOGEN COMPOUNDS

CHAPTER VIII

MANUFACTURE OF FERROCYANIDES

SOME time after the discovery of Diesbach, that a blue colouring-matter could be obtained by adding an iron salt and an acid to solution of the melt obtained by fusing potassium carbonate with dried blood, the colour was made on a commercial scale and put on the market as a substitute for ultramarine. Macquer, in the middle of the eighteenth century, had shown that potassium ferrocyanide could be obtained by treating the blue with potash and evaporating the clear solution, when crystals of the ferrocyanide separated on cooling. These crystals were called by him "phlogisticated alkali." It was afterwards shown that this compound existed in the lixiviated melt before precipitation of the blue.

As the colouring-matter became better known its demand increased, and the manufacture of potassium ferrocyanide became a growing industry. Dried blood was at first the only nitrogenous material used, but afterwards hoofs and horns, wool and leather, were used as well, sometimes singly, sometimes a mixture

of two or more, according to the individual fancy of the manufacturer.

The potash was put into an iron pot fixed in a furnace and fused, the dried blood or other nitrogenous matter introduced a little at a time, in order to prevent excessive frothing. When the material in the pot began to thicken and become pasty, owing to the large amount of carbon derived from the charred organic matter, the operation was stopped, the charge ladled out of the pot, and when cold broken up and dissolved in water. The aqueous solution had a green colour due to the formation of a double potassium iron sulphide, this sulphide being formed by the reduction of the potassium sulphate, always present in the impure potassium carbonate used, and the sulphur of the organic matter.

After filtration, or decantation, the solution was allowed to cool, when crude crystals of potassium ferrocyanide crystallized out, which were purified by recrystallization. The mother liquor, which still contained a considerable quantity of ferrocyanide, was further concentrated to obtain a second crop; and, finally, evaporated to dryness and ignited. A portion of these ignited salts known as " blue salt," consisting principally of carbonate of potash, was used with fresh alkali for each melt.

In the early theories of the formation of the ferrocyanide, it was considered that the ferrocyanide existed in the melt in the molten state in the furnace. It was, however, afterwards shown that ferrocyanides were destroyed when fused with an alkali, and that the earlier theories were incorrect. The nitrogen of the organic matter combines with the alkali and carbon to form potassium cyanide; and when the melt is lixiviated with water, the cyanide reacts with the green iron double sulphide to form ferrocyanide. This green iron sulphide was, therefore, essential in the formation of ferrocyanides by this process. As the sulphide of iron was formed at the expense of the iron of the pot, the life of one of these pots, though

made of very thick cast iron, was comparatively short; and in order to prevent the corrosion of the vessel, it subsequently became the practice to add scrap iron to the melt during fusion, and increased yields of prussiate were obtained; for the reason that the sulphur either combined with the iron or the cyanide, and if insufficient iron was present, thiocyanates were formed.

The excessive foaming of the molten salts when the organic matter was introduced, was a great difficulty of the process, and many efforts were made to remedy it. By charring the organic matter before adding it to the molten alkali most of the frothing was overcome, but this method was not economical, as a comparative large percentage of the nitrogen was lost in the preliminary operation.

Many attempts were made to substitute sodium carbonate for the potassium salt, but apparently without success, for all such attempts when tried were finally abandoned; and it was stated that when used either alone or in conjunction with potash, much lower yields were obtained.

It was necessary that the animal matter when added to the melt should be free from moisture, otherwise the water would attack the potassium cyanide already formed in the molten mass and convert it into ammonia which was lost. A portion of the nitrogen of the organic matter was always lost in the form of ammonia, and a greater quantity was lost in this form if too large an amount of animal matter was added at one time, owing to the consequent drop in temperature. The recovery of the nitrogen lost as ammonia occupied a good deal of attention, and experiments were conducted in one case to convert it into cyanide by passing the ammonia over an ignited mixture of potassium carbonate and charcoal, but they were not commercially successful.

Bower [1] proposed to introduce ferric thiocyanate in small portions towards the end of the fusion in order to obtain an increased yield of cyanide in the melt.

[1] E.P. 8381, 27.4.95.

The type of pot first used in this industry was pear-shaped, but subsequently shallow rectangular trays set in a furnace were substituted; each furnace was capable of dealing with five to six charges a day. This process was never an economical one, only about one-sixth of the total nitrogen of the organic matter was obtained as prussiate, and great losses of potassium carbonate occurred, owing to the formation of silicate, etc.

With the recovery of ferrocyanides from gas purification refuse and the introduction of cheaper methods of manufacturing cyanides, this process for the manufacture of prussiates from animal matter passed out of use in Europe. The process was, however, until quite recently carried on in the United States of America.

Owing to the difficulties of the fusion process other sources of nitrogen were sought, and about the middle of the nineteenth century Possoy and Boissierre erected a factory near Paris to manufacture yellow prussiate of potash by passing the nitrogen of the air over a strongly ignited mixture of potassium carbonate and carbon. The charcoal impregnated with potassium carbonate was placed in earthenware retorts, and heated to a white heat for about ten hours, during which time a current of air was passed through. Owing to the very high temperature required, the consumption of fuel was excessive, and the manufacture was afterwards transferred to Newcastle in order to cheapen the cost of fuel. There the process was subsequently modified, and ground iron ore added to the mixture in the retorts, the product was emptied from the retorts, lixiviated, and the solution crystallized in much the same way as the older prussiate process. This factory was in work two years, and is said to have produced about one ton of yellow prussiate per day. The process was not found to be a commercial success, the cost of fuel being excessive, and the life of the retorts short, they being unable to withstand the very high temperature to which they were subjected.

Margueritte and De Sourdeval substituted barium oxide for the carbonate of potash, and have shown that barium cyanide can be easily formed by passing air over barium oxide and carbon heated to a bright red heat. As the oxide does not fuse, it has this advantage over potassium carbonate, for the nitrogen is brought into more intimate contact with the alkali. It was at one time thought that as the outcome of the above process, barium ferrocyanide would be the commercial substitute for the potassium salt; these hopes were, however, never realized, and in later years sodium ferrocyanide has to a very great extent taken the place of the potassium salt.

Many attempts were made and much money spent on these efforts to manufacture cyanides, and consequently ferrocyanides, from the nitrogen of the air, by passing this gas over heated alkali in contact with carbon; and a great number of patents were taken out for more or less improvements, but in spite of all efforts these methods have not yet become commercially successful.

The existence of cyanogen compounds in coal gas had been demonstrated as long ago as the middle of the nineteenth century, but it was not until the introduction of oxide of iron as a purifying agent, in which appreciable quantities of cyanogen were arrested in the form of complex blue iron cyanogen compounds, that any real effort was made for their recovery; and then only by very unscientific and crude methods.

After the successful application of the MacArthur and Forest process for the extraction of gold from its ores, by the action of a dilute cyanide solution, the demand for this material greatly increased, and attention was directed to cheap methods of manufacture, and cheap raw material; and the problem of their recovery from the waste material of the gas works attacked in a somewhat more scientific manner.

In the process of coal-gas purification the sulphuretted hydrogen is removed by passing the gas through a series of purifiers containing layers of bog

ore, or other iron oxides, of about 14 in. thick; the sulphuretted hydrogen reacts with the oxide to form iron sulphide. When no more sulphur is absorbed, the oxide is taken out of the purifier and exposed to the air to "revivify"; during this operation it absorbs oxygen from the air, sulphur is set free, and the oxide of iron regenerated. It is then put back into the boxes to be again fouled with sulphuretted hydrogen from the crude coal-gas. These series of operations are repeated until the percentage of free sulphur amounts to from 40 to 50 per cent., at which stage the oxide is so covered by material absorbed from the gas that its function as a purifying agent is too much retarded to be of any further value. This fouled or "spent" oxide, as it is generally called, is then thrown out of use, and replaced by fresh material.

The coal-gas also contains, as mentioned above, small quantities of hydrocyanic acid, which, coming into contact with freshly formed ferrous sulphide, reacts in conjunction with a little ammonia with formation of ferrous ammonium ferrocyanide, thus :

$$6HCN + 2NH_3 + 2FeS = Fe(NH_4)_2Fe(CN)_6 + 2H_2S.$$

When the oxide is exposed to the air for the purpose of revivification, this compound, surrounded by ferrous sulphide, is slowly oxidized, partly into various blue ferric ammonium ferrocyanides and partly into the green ferrosoferric ammonium ferrocyanide, thus :

$$(1)\ 44Fe''(NH_4)_2Fe(CN)_6 + 22O = 4Fe'''_{11}(NH_4)_3[Fe(CN)_6]_9 + 8(NH_4)_4Fe(CN)_6 + 44NH_3 + 22H_2O.$$

$$(2)\ 16Fe''(NH_4)_2Fe(CN)_6 + 3O_2 = 4Fe'''_2Fe''(NH_4)_3[Fe(CN)_6]_4 + 2Fe_2O_3.$$

The free ammonium ferrocyanides formed in the first equation are rapidly converted into insoluble blue compounds by reaction with unaltered ferrous sulphide or basic ferric sulphate.

A small quantity of free ammonia is essential in order to absorb the cyanogen in the oxide boxes, for if gas containing hydrocyanic acid but quite free from ammonia is passed over freshly prepared ferrous

sulphide, also free from ammonia or other alkali, no action takes place, the hydrocyanic acid passing over unchanged. If a little ammonia is introduced and allowed to pass over the sulphide, an immediate action takes place, with the formation of ferrous ammonium ferrocyanide, and evolution of sulphuretted hydrogen or ammonium sulphide.

An excess of ammonia, however, is a great error when the oxide has been once revivified and contains free sulphur; and would result in the formation of a large amount of thiocyanates at the expense of the ferrocyanides. The ammonia and sulphuretted hydrogen would first be condensed in the moisture of the spent oxide as ammonium sulphide, and rapidly dissolve sulphur, forming ammonium polysulphide, which would react in contact with the hydrocyanic acid to form ammonium thiocyanate. In fact, by allowing an excess of ammonia to pass, and keeping the oxide very moist, all the hydrocyanic acid can be arrested in the form of ammonium thiocyanate: [1]

(1) $2NH_3 + H_2S + S_2 = (NH_4)_2S_3$.
(2) $(NH_4)_2S_3 + 2HCN = 2NH_4CNS + H_2S$.

The amount of ferrocyanides in a spent oxide made in this country will vary from a trace to 6 or 7 per cent. calculated as $Fe_7(CN)_{18}$, and but seldom exceed this figure, though much higher values are met with on the continent.

A great deal of attention has been paid in the past years to the problem of profitably extracting the ferrocyanides from the spent oxides, and much time and money has been spent, but few cases in this country have been commercial successes.

The difficulties of the problem are many, the great cost of labour and plant necessary to handle the very large bulk of material, which contains only a few per cent. of ferrocyanides, and the extraordinary difficulty of decomposing and recovering the ferrocyanide complex in the spent oxide. A difficulty enormously

[1] P. Williams, E.P. 23,604 (1909).

increased by the presence of free sulphur, which if not completely removed before attempting to extract the ferrocyanides with alkalis, would pass into solution combined with the alkali as polysulphide; and not only neutralize, and therefore waste, some of the alkali, and greatly retard further extraction, but convert some of the ferrocyanides into thiocyanates with consequent loss. Subsequently attempts were made to extract the sulphur first, before attempting to recover the ferrocyanides. Various solvents were proposed, and a number of patents taken out to accomplish this, with some little measure of success: but here again a great difficulty was encountered, as all the solvents used were equally good solvents for tar as for sulphur; and consequently the sulphur when recovered was of varying shades of brown to black, due to the tar dissolved with it, thus rendering it practically unsaleable for any other purpose than burning for sulphuric acid making, and at a price per unit of sulphur but little above that of the untreated spent oxide. Endeavours to purify the sulphur in a simple manner and at a reasonable cost met with practically no success.

Thus the cost of extracting the sulphur from the spent oxide did not pay for itself, but was an added cost on the ferrocyanide extraction.

As the methods of extraction improved and became more economical and efficient, the price of cyanides and ferrocyanides dropped considerably; and also owing to the successful introduction of synthetic methods for the making of cyanides, the demand for ferrocyanides decreased accordingly, thus this industry never became a very successful one.

Another great difficulty was that to be successful demanded a plant of large capacity, fitted with all possible labour-saving devices; but to supply the material to keep such a plant working necessitated going very far afield to obtain material rich enough in ferrocyanides to pay for the working; and the carriage on such bulky material when 100 tons had to

be handled in order to obtain 6 to 7 tons of prussiate was an extra and heavy burden.

It was, of course, necessary to obtain spent oxides as rich in ferrocyanides as possible, for whatever the ferrocyanide contents the carriage and cost of handling were the same ; thus for a spent oxide low in ferrocyanides, the output of manufactured prussiate would be correspondingly low, but the cost of working and the amount of spent oxide handled per week practically the same as for a rich spent.

In order to overcome some of the difficulties of spent oxide extraction, considerable attention was directed to scrubbing the gas with the object of extracting the ferrocyanides only, in order to obtain a more compact product richer in ferrocyanides. To these ends a solution containing precipitated ferrous hydroxide in suspension in the presence of an alkali, such as sodium or potassium carbonate, or free lime, or merely a solution of ferrous sulphate using the ammonia in the gas as the alkaline base, was placed in specially designed scrubbers and the crude gas passed through. These methods met with varying success, and with some modifications are being worked at the present time.

Recently a method of recovery has been proposed [1] in which the crude gas is led up a tower packed with Cleveland iron ore, and down which a suitable alkaline liquid is made to flow, a solution of ferrocyanide being drawn away at the bottom.

Coal contains 1 to 1.7 per cent. of nitrogen, of which only about 1½ or at most 2 per cent. in favourable cases is converted into hydrocyanic acid. It has, however, been estimated that if this amount were reasonably recovered, enough cyanogen compounds would be formed to far more than supply the world's demand for cyanides.

Some idea of the great difficulty of recovering this cyanogen can be obtained when it is remembered that here on the one hand, the cyanogen compounds exist

[1] W. H. Coleman, E.P. 27,908 (4/12/12).

ready formed, and their removal is an advantage to the gas; yet it has been found possible to make synthetic cyanides from such expensive materials as ammonia and metallic sodiums, not only to compete with the product from the gasworks, but to lower the price and to capture the bulk of the world's trade.

Although the difficulties of this problem are great, still there can be but little doubt that, had it been attacked in a reasonably scientific manner, the gas undertaking would to-day have held the control of the cyanide market. The reason of this failure is due to the policy still pursued in the gas world, of placing difficult and intricate chemical problems in the hands of an engineer who, though highly skilled and capable in his own particular line, is yet quite incapable of dealing with problems of this nature.

CHAPTER IX

MANUFACTURE OF FERROCYANIDES

From Spent Oxide of Iron. The various methods for extracting the ferrocyanides from spent oxide may be classed under two heads, viz. :

1. Extraction by alkali in the presence of the sulphur.
2. Extraction after the removal of free sulphur.

The fouled or spent oxide of iron is in reality a very complex mixture of a large number of bodies, and an analysis of a fair average sample of English spent oxide is given below.

	Per cent.
Free sulphur	44.70
Moisture	17.88
Ferric monohydrate	5.26
Ferrous monohydrate	6.25
Basic ferric sulphate	1.25
Ferric ammonium ferrocyanide	3.80
Ferrosoferric ammonium ferrocyanide	2.50
Ferric pyridic ferrocyanide	1.20
Organic matter peat fibre	4.68
Tar	1.21
Silica	1.05
Naphthalene	0.72
Pyridine sulphate	0.77
Ammonium sulphate	2.06
Calcium sulphate	0.12
Ferrous sulphate	0.02
Ammonium thiocyanate	1.30
Sulphur otherwise combined	1.33
Organic matter soluble in alkalis (humus)	1.54
Combined water and loss (by difference)	2.36
	100.00

In the earlier methods of extraction, the spent oxide was simply mixed with an excess of slaked lime, and leached with water, or weak solutions obtained in previous operations. The liquor, which contained calcium ferrocyanide and thiocyanate, was acidified with hydrochloric acid and precipitated with an excess of ferric chloride solution, and the blue precipitate filtered and washed. The blue so obtained was, of course, very impure, and contained free sulphur as well as tarry and other organic impurities. In 1878 a patent was taken out to improve the quality of this blue [1] by extracting with 90 per cent. benzol in an extraction apparatus to remove the tarry compounds and improve the colour. If the material contained free sulphur, carbon disulphide was first used, followed by the benzol. The blue, although of course considerably improved in appearance by this treatment, was still greatly inferior as a pigment to that obtained from pure potassium ferrocyanide.

This process of extraction was later much improved upon, the spent oxide was placed in large leaching tanks, each fitted with a false bottom, and washed with water to remove soluble ammonium salts. These tanks were usually arranged in batteries of from six to eight, and were best made of wood, on account of the excessive corrosive action of the solution of ammonium salts. The tanks were washed in series, that is the weak liquor from one tank was placed on the next, and so on, to obtain as strong a liquor as possible, the spent being first washed with weak liquor and finally with water. The strong liquor, which contained a considerable quantity of ammonium salts, was distilled with lime, and the ammonia converted into ammonium sulphate.

The thoroughly washed spent oxide, which had then turned a blue or bluish-green colour, was removed from the tanks and mixed with about 10 per cent. of slaked lime—according to the spent oxide—and spread out on a drying-floor, where it was repeatedly turned

[1] W. V. Wilson, E.P. 314 (1878).

over with a shovel : during this operation most of the ammonia fixed or combined with the ferrocyanide was liberated and escaped. When the mixture was fairly dry, and the colour had changed from a bluish-green to a light brown, it was then placed in a second battery of tanks of somewhat larger capacity and again systematically washed with water or weak liquor from previous operations.

It was soon found, however, that the advantage of the preliminary washing was more than counter-balanced by its expense, as only a portion of the ammonia in the spent oxide was soluble in water, and this stage of the process was consequently abandoned.

In the modified method, the spent oxide was sifted, the lumps ground and the whole mixed with quicklime or a mixture of quick and slaked lime, the oxide being moistened if necessary, and the whole well mixed and placed in leaching tanks. By the use of quicklime the temperature of the mixture was raised, thus assisting the reactions.

The liquor obtained by leaching the limed spent oxide was of a light or dark brown colour, depending on the composition of the spent oxide used, and contained calcium ferrocyanide and thiocyanate in solution as well as free ammonia and sometimes poly-sulphide and thiosulphate of calcium.

This liquor was very crude and needed purification, which was generally accomplished by neutralizing the liquid with hydrochloric acid and boiling, when a sparingly soluble crystalline precipitate of the double calcium ammonium ferrocyanide was obtained. If the liquor did not contain sufficient ammonium chloride to precipitate all the ferrocyanide, the calculated quantity of the ammonium chloride necessary was added :

$$Ca_2Fe(CN)_6 + 2NH_4Cl = Ca(NH_4)_2Fe(CN)_6 + CaCl_2.$$

The insoluble double salt was either separated by decantation or by means of a filter press, preferably the latter. Then mixed with water and a slight excess of slaked lime and boiled in a closed receiver, the

ammonia being recovered as the chloride by absorption in hydrochloric acid solution, and the sludge filter-pressed :

$$Ca(NH_4)_2Fe(CN)_6 + CaO = Ca_2Fe(CN)_6 + 2NH_3 + H_2O.$$

The clear liquor from the filter-press consisted of an almost pure solution of calcium ferrocyanide and was converted directly into the sodium salt by boiling with the calculated quantity of sodium carbonate, filtered from the precipitated carbonate of lime, and the filtrate evaporated and crystallized.

If it was required to make the potassium salt, the crude solution of calcium ferrocyanide was boiled with the requisite quantity of potassium chloride to precipitate the ferrocyanide as the sparingly soluble calcium potassium ferrocyanide :

$$Ca_2Fe(CN)_6 + 2KCl = CaK_2Fe(CN)_6 + CaCl_2,$$

and the precipitate washed by decantation. For this purpose it was not necessary to purify the ferrocyanide solution by means of the double ammonium salt, but to use the crude liquor after all the free ammonia had been boiled off. The washed double salt was then boiled with potassium carbonate to remove the remaining calcium from the ferrocyanide and the solution of potassium ferrocyanide filtered from the carbonate of lime, evaporated and crystallized.

The reason that two operations were used to convert the calcium ferrocyanide into the potassium salt was to lessen the cost of the potassium salts, potassium chloride being only about half the price of the equivalent of potassium carbonate.

The results obtained by the above methods were never good, from 1 to 1½ per cent. of the ferrocyanide being left unattacked in the thoroughly washed spent residue. The reason of this loss was twofold : first, owing to the process of the formation of the spent oxide, it consisted of various sized irregular-shaped pellets, built up by a series of concentric deposits, which it was impossible for the alkali completely to penetrate ; and thus a small portion of the blue was

left unacted on in the core of these pellets. The second reason was a little more deep-seated, part of the blue in the spent oxide was combined as the ferrosoferric ammonic ferrocyanide, a very stable and complex body which was only partially decomposed by the slaked lime thus :

$$Fe'''_2Fe''(NH_4)_8[Fe(CN)_6]_4 + 6CaO = 3Ca_2Fe(CN)_6 + Fe_2O_3 + Fe(NH_4)_2Fe(CN)_6 + 6NH_3 + 3H_2O.$$

The ferrous ammonium ferrocyanide was undecomposed by the lime, and therefore left in the spent oxide; this body became partially oxidized in the earlier processes when the washed spent was mixed with lime on a drying floor and exposed to the air for some time, but the extra cost of this operation was greater than the extra value of the extraction.

The first difficulty could be overcome by grinding the spent to a fine powder, but the sludge so obtained was impossible to leach, and it was necessary to employ filter-presses. The spent oxide was ground to a fine sludge with weak liquor from a previous operation in any suitable type of wet mill, and then run into a large tank fitted with beaters which kept the liquid agitated while the necessary quantity of ground quicklime or slaked lime was added, and the sludge filter-pressed and washed.

This, however, did not get over the second difficulty, but it was afterwards found that the addition of sufficient sulphate of sodium reduced the unextracted portion of the ferrocyanide to a minimum, and practically complete extraction could be obtained by grinding the spent oxide to a fine sludge with weak liquor and the necessary quantity of sulphate of sodium. Then while keeping the mixture well agitated, the lime was slowly added. Great care was necessary in this operation, for if excess of lime was added, or if the lime was added at too great a rate, some polysulphide appeared in solution, which greatly retarded further extraction and in many cases attacked some of the unextracted ferrocyanide with formation of thio-

cyanates. The sulphate of sodium could be added to the mill along with the spent oxide in the form of salt waste or nitre cake, together with the necessary quantity of lime to neutralize the sulphuric acid.

The exact function of the sodium sulphate was never fully explained, though it may perhaps have been due to the fact that it removed the greater part of the calcium salts from solution and thus prevented the formation of insoluble basic calcium ferrocyanides. Double decomposition also took place to a certain extent with the ferrous ammonium ferrocyanide :

$$Fe(NH_4)_2Fe(CN)_6 + Na_2SO_4 \rightleftharpoons FeNa_2Fe(CN)_6 + (NH_4)_2SO_4.$$

This double sodium ferrous ferrocyanide was more readily decomposed by the lime.

The addition of sodium chloride also improved the extraction by lime, but not to so great an extent as the addition of sodium sulphate.

Ferrocyanide extraction after first removing the sulphur. In order to obtain better extraction of the ferrocyanide from spent oxide, attempts were made to remove the sulphur first. A large number of solvents have been advocated for this purpose, such as carbon disulphide, toluol, benzol, light petroleum oils, acetylene tetrachloride, orthodichlorbenzene, creosote oil, and ammonium sulphide.

Carbon disulphide is the solvent most generally used, and at first was the only one. The spent oxide, which should not contain more than 10 to 12 per cent. of water, is placed in a closed extraction vessel without grinding, the carbon disulphide added at the top and allowed to percolate through the material until all the sulphur is removed, the sulphur being very soluble in this solvent in the cold. The sulphur solution is then evaporated and all the solvent driven off, and condensed for reuse in the extraction vessel.

When all the solvent has been driven off, the temperature of the still, which is surrounded by a steam jacket, is raised, and the sulphur melted and run out. Steam is also blown through the sulphur

extracted oxide to drive off all the solvent wetting the material, which is then dug out of the extractor and treated for the recovery of the ferrocyanides, by dilute caustic soda solution or by lime and sulphate of soda as previously described.

Though bisulphide of carbon is an excellent solvent for sulphur, it is a somewhat dangerous solvent to use on account of its extreme volatility and its low ignition temperature when its vapour is mixed with air, contact with a high-pressure steam-pipe being sufficient to ignite the mixture.

A modification of the above method was proposed, by which the process became continuous.[1] The sulphur-saturated carbon disulphide was allowed to flow slowly on to the surface of water maintained at a temperature of 70° C., in a closed vessel, fitted on the top with an outlet vapour-pipe connected to a condenser. The solvent was immediately evaporated as the liquid touched the surface of the hot water, and passed away up the vapour-pipe to the condenser, while the solidified sulphur settled to the bottom of the water quite free from solvent. When sufficient sulphur had accumulated it was removed by running off the water and emptying the sulphur through a manhole. By this method the dangers of explosion were greatly decreased and much less solvent was needed in circulation.

The advantage of the use of toluol, benzol or light petroleum oils, etc., of which perhaps toluol is the best, is that though these solvents readily dissolve sulphur when heated, practically the whole is deposited when the solution is cooled. The amount of sulphur dissolved by the solvent varied with the temperature, and increased as the temperature rose.

The fact that sulphur was sparingly soluble in these solvents when cold offered a great advantage over the use of carbon disulphide, from the fact that it was not necessary to distil the whole of the solvent in order to obtain the dissolved sulphur. All that was necessary

[1] Max Rohleder, E.P. 23,967 (1906).

was to cool the solution when 90 to 95 per cent. of the sulphur was deposited in the form of sparkling crystals, and the solvent decanted off for further use.

The method of working with this solvent differed somewhat from that previously described for bisulphide of carbon. The toluol was added to the spent oxide, which may contain as much as 14 per cent. of water, in a steam-jacketed vessel fitted with mechanical agitators and heated with the solvent until the temperature of 100° to 110° C. was attained, and stirred from ten to fifteen minutes. It was then allowed to settle—which the presence of water introduced with the spent materially assisted by binding together the partially extracted residue—and the clear liquor decanted off by means of a lixiviating valve, passed through a steam-heated filter into a vacuum cooler having a cone-shaped bottom. The solvent boiled violently under reduced pressure, and consequently quickly cooled and deposited the sulphur in fine crystals. When the liquid was cold, the clear liquid was decanted off into the storage tanks for reuse and the sulphur sludge dropped out of the cone-bottom of the cooler, by opening a large sludge valve into a vacuum filter, and drained; steam was then blown through from the bottom to remove the last traces of the solvent.

These operations were repeated until the spent in the extraction vessel was free or practically free from sulphur, and three or at most four washes were all that were necessary; the solvent left wetting the cake was removed by steam distillation. The residue was then mixed into a thin paste with some weak ferrocyanide liquor or mother liquor, and blown over into a second vessel to extract with lime and sulphate of sodium, or if cheap alkali was obtainable, with caustic soda in the usual manner.

The use of creosote oil scarcely needs mention, although it has been suggested for use for this purpose. It is true that this oil is an excellent solvent for sulphur when hot, and that it is quite easy to separate the

sulphur from the spent oxide by its means, yet it is practically impossible to separate the black oil wetting the recovered products without the use of volatile solvents.

The application of ammonium sulphide as a solvent for sulphur was of quite a different nature to those described above, as this solvent was worked in aqueous solutions and was non-inflammable.

The principle of the process depended on the fact that ammonium sulphide or ammonium sulphydrate readily dissolves sulphur to form ammonium polysulphide, and that the filtered ammonium polysulphide solution is decomposed on boiling ammonium sulphide, distilling off with precipitation of the dissolved sulphur. The solution of the sulphide or polysulphide did not dissolve or destroy any of the ferrocyanide contents of the spent oxide.

It is doubtful whether this process is or has been worked on a commercial scale, although during the years 1906 and 1907 the author had some considerable experience of this process on a small-scale experimental plant.

The spent oxide may be either agitated in a vessel with an excess of ammonium sulphide and filtered, or the solvent allowed to percolate through the oxide in an extraction apparatus, until all the sulphur is dissolved out; but the former method is on the whole to be preferred. The extracted residue is then washed with water, and the wash-water added to the main bulk of sulphur liquor.

The sulphur liquor, consisting essentially of ammonium polysulphide together with small quantities of ammonium sulphate and thiocyanate, is then boiled in a closed vessel connected by a wide vapour-pipe to a condenser. The ammonium polysulphide breaks up on boiling into ammonia and hydrogen sulphide, which are carried off by the steam and condensed as a solution of ammonium sulphide, while a precipitate of sulphur is left behind in the still with the surplus water :

$$(NH_4)_2S_5 = 2NH_3 + H_2S + S_4.$$
$$2NH_3 + H_2S = (NH_4)_2S.$$

It is necessary that during the distillation a small trickle of water or weak liquor should be passed through the condenser to prevent any blocking of the tubes by the crystallization of the ammonium sulphide.

When the whole of the ammonium sulphide has been distilled off, the liquid containing the precipitated sulphur is filtered either by running it on to a vacuum filter or by means of a filter-press and washed. The sulphur so obtained is practically free from tar, but is coloured slightly brown from the presence of organic matter soluble in the alkaline solution. A great proportion of this brown colouring-matter may be prevented from passing into solution by the addition of certain salts, particularly calcium chloride, to the ammonium sulphide solution before extraction of sulphur. A very pure sulphur may be obtained by dissolving the recovered sulphur in carbon disulphide—in which solvent the organic colouring-matter appears to be insoluble—and evaporating the solvent off.

The extracted oxide, after washing free from ammonium sulphide, is boiled with caustic soda solution or with lime and sulphate of sodium to recover the ferrocyanide, the ammonia which distils off being absorbed in sulphuric acid and recovered as ammonium sulphate.

None of the ferrocyanides are destroyed by the above treatment, and in fact if all the sulphur is removed as high ferrocyanide yields can be obtained as when the sulphur is extracted by carbon disulphide.

When the ammonium sulphide is added to the spent oxide some of the solvent is destroyed by reactions with a portion of the iron of the ferrocyanides, and the basic ferric sulphate always present in a spent oxide. This loss of ammonium sulphide can be readily made good by adding some calcium polysulphide solution to the sulphur liquor before boiling off the ammonium sulphide. The calcium polysulphide is easily prepared by boiling a little of the precipitated sulphur with

lime ; it reacts with the ammonium sulphate in the liquor thus :

$$CaS_5 + (NH_4)_2SO_4 = CaSO_4 + (NH_4)_2S_5.$$

To counteract any ammonia losses which may occur, sufficient calcium polysulphide should be added to form ammonium sulphide with the ammonium thiocyanate and sulphate in the spent oxide :

$$CaS_5 + 2NH_4CNS = Ca(CHS)_2 + (NH_4)_2S + S_4.$$

This calcium thiocyanate would be left in solution in the filtrate from the sulphur.

One of the great drawbacks of this process which prevented its application on a large scale, was the difficulty of filtering the extracted oxide, owing to the formation of ferrous sulphide by the above-mentioned reactions.

The sulphur obtained by the use of organic solvents was always contaminated with tar, and a number of methods were proposed to purify it. Re-solution in pure bisulphide of carbon and fractional crystallization yielded a first crop of comparatively pure sulphur, but a large quantity of sulphur was left in solution, with the accumulated tar, which it was difficult to purify. A pure solution could, however, be obtained by passing the tarry sulphur liquid through animal charcoal, but this method was much too expensive as a large portion of animal charcoal was necessary, and wood charcoal was useless.

In the method of distillation, the sulphur was first melted in a large-sized iron pot and heated slowly to 600 to 700° C. and kept at that temperature for four to five hours. During this operation very considerable frothing took place, part of the organic matter distilled off, and the remainder reacted with the sulphur to form carbon disulphide and hydrogen sulphide. When this action ceased, the temperature was raised and the sulphur distilled off and collected either as flowers or rock sulphur.

As the importance of prussiates and cyanides

became more evident a number of synthetical methods for making cyanides were brought into operation and worked with success. The price, however, of these products for a number of causes fell, and it therefore became evident that more efficient methods of recovering the hydrocyanic acid from coal-gas were necessary if the gas undertakings were to have any share in the production of cyanide compounds.

Only about 50 to 60 per cent. of the cyanogen in the crude coal-gas was arrested in the spent oxide, and the difficulties of recovering this valuable material from the complex spent oxide has already been explained. Great efforts were therefore made to obtain a product richer in cyanogen contents by scrubbing the gas with certain solutions for the removal of the hydrocyanic acid only.

Knublauch [1] patented a process for the use of a solution of ammonia or other alkali, containing in suspension the hydroxide or carbonate of iron, zinc or manganese, for the absorption of hydrocyanic acid in the gas. But only the suspensions containing iron in the form of ferrous hydroxide or carbonate were found to be of any value, as no cyanogen compound of zinc or manganese could be formed in the presence of a large excess of hydrogen sulphide, such as existed in the crude coal-gas.

This process did not make much headway at first, and was followed by the Foulis process.[2] According to this method, ferrous sulphate solution is exactly precipitated with sodium carbonate, and the precipitate freed as much as possible from sulphate of sodium by washing with water. The ferrous carbonate is then suspended in a solution of sodium carbonate, the mixture placed in specially designed scrubbers, and the gas bubbled slowly through. This process was adopted by several of the large gas companies, but was at first placed after the ammonia scrubbers. The object of this was an attempt to obtain all the ferro-

[1] E.P. 15,164 (1887).

[2] E.P. 9474 (1892), and 15,168 (1895).

cyanides in the form of the soluble sodium salt, for if much ammonia were present the insoluble ferrous ammonium ferrocyanide would be formed, which is not decomposed by sodium carbonate.

These expectations were, however, never realized with this process; the sludge always contained both the soluble sodium ferrocyanide and some insoluble ferrous sodium ferrocyanide. In view of this fact, and also that some considerable amount of hydrocyanic acid was removed by the ammonia scrubbers, the position of the cyanide washer was changed, and placed before the ammonia scrubbers. Another advantage of this position was that the ammonia of the gas maintained the alkalinity of the liquid, and practically all the hydrocyanic acid was absorbed, whereas in the former position the alkali decreased towards the end of the operation and some of the cyanogen compounds were undoubtedly thus lost.

When worked in this position the fouled liquor contained ferrous sodium and ferrous ammonium ferrocyanide in suspension, together with the excess ferrous sulphide and some tar, and sodium ferrocyanide and sulphide in solution.

The fouled sludge, when it had absorbed the maximum amount of hydrocyanic acid, was withdrawn from the scrubber and boiled to recover the volatile ammonia after the addition, if necessary, of more sodium carbonate, and filter-pressed. This preliminary boiling operation materially affected the subsequent filtration, for the liquid, which before boiling was practically unfilterable, was after boiling much more easily filtered, as the suspended matter became more flocculent. The clear filtrate was carefully evaporated, and cooled to obtain crystals of sodium ferrocyanide. The double ferrous ferrocyanides in the sludge, although unattacked by the carbonates of sodium or potassium even at the boiling temperature, are readily attacked in the cold by caustic alkalis. The cake from the filter-press was therefore treated with 90 per cent. of the calculated quantity of caustic soda necessary

to decompose all the insoluble ferrocyanide, after mixing the cake to a thin sludge with water. It was considered an unnecessary operation to filter to recover the soluble ferrocyanide at this stage, so the sludge was put back into the scrubber together with the necessary amount of sodium carbonate and fresh ferrous carbonate.

This process was in use with more or less success for some time with various alterations in detail, though not in principle. The use of lime as an alkali was proposed and used, and in at least one works on the Continent carbonate of potassium was used in place of the sodium salt and the cyanogen recovered as potassium ferrocyanide.

The main objection to this process and its modifications was that it was impossible to obtain the ferrocyanide in one condition only, as both soluble and insoluble ferrocyanides always existed in the same sludge.

Dr. Bueb patented a process [1] whereby this difficulty was overcome. Finding that it was practically impossible to obtain all the ferrocyanide in solution, he attacked the problem from the other side, and succeeded in working out a process whereby he obtained all the ferrocyanide in the insoluble form. The advantage of such a process is obvious, for on filter-pressing the cake all soluble impurities are removed in one operation. In this process the only alkali used is the ammonia existing in the crude gas. A solution of ferrous sulphate is placed in a specially designed washer divided into a number of bays, and the liquor pumped from one to the other in succession. The solution in the first bay meeting gas free from hydrocyanic acid, but still containing a considerable proportion of sulphuretted hydrogen and ammonia, reacts, forming ferrous sulphide and ammonium sulphate. This liquor, as it passes on through the successive sections of the scrubber, comes in contact with the hydrocyanic acid of the gas, with

[1] E.P. 9075 (1898).

which it reacts, forming ferrous ammonium ferrocyanide :

$$2FeS + 2NH_3 + 6HCN = Fe(NH_4)_2Fe(CN)_6 + 2H_2S,$$

and possibly also some ammonium ferrous cyanide :

$$FeS + NH_3 + 3HCN = NH_4Fe(CN)_3 + H_2S.$$

When the finished liquor is pumped out of the last section of the scrubber, practically the whole of the ferrous sulphide should have entered into the above reaction, and the liquor after the sludge has settled is of a yellow or reddish-yellow colour. If the sludge has been left in the scrubber too long some ammonium ferrocyanide is formed in solution, which, however, is easily removed by the addition of a little ferrous sulphate solution. The sludge is then boiled to drive off all volatile ammonia, and filter-pressed. The cake is mixed with dilute caustic soda or preferably lime, and boiled to decompose the insoluble ammonium ferrocyanide, the evolved ammonia being absorbed in sulphuric acid. When all the ammonia has been driven off, the liquid is pumped through a filter-press. The clear filtrate which contains the whole of the ferrocyanide in the form of the sodium or calcium salt, according to the alkali used, is in the latter case treated with carbonate of sodium and filtered, and the solution concentrated to recover the crystals of sodium ferrocyanide. This evaporation, which should be performed under reduced pressure, is usually accomplished by boiling in open pans at atmospheric pressure, with the consequence that some slight loss of ferrocyanide by decomposition occurs.

The washed insoluble cake from the filter-press, which consists almost wholly of ferrous hydroxide and sulphide, is sludged up with more water, avoiding oxidation as much as possible, and returned to the cyanogen scrubber.

Some earlier attempts had been made to work without the addition of an alkali, but to use the ammonia of the gas for this purpose ; these processes, however,

aimed at a solution of ammonium ferrocyanide by working with very dilute solutions of ferrous salts. Practically the first attempt in this direction was made in 1892, when Rowland endeavoured to absorb all the hydrocyanic acid in the ammonia scrubbers by adding an iron salt in quantities insufficient to form ferrous sulphide. The liquor then, after distilling off the ammonia, was precipitated with ferrous sulphate, the precipitate boiled with lime, and the ferrocyanide recovered as the potassium salt, by first forming the sparingly soluble double salt, by boiling with potassium chloride, and decomposing the washed double salt with potassium carbonate.

As the ferrocyanide is manufactured principally for conversion into sodium cyanide, a method more economical than those described above would be to convert the insoluble ferrous ammonium ferrocyanide contained in the filter-press cake obtained in Bueb's process directly into the cyanide, and thus save the cost of conversion and also the loss incidental to that operation.

It would be quite possible to accomplish this by distilling the filter-pressed cake with dilute sulphuric acid and a little cuprous chloride and absorbing the evolved hydrocyanic acid in caustic soda solution.

The filter-press cake must first be mixed with water and sufficient dilute sulphuric acid added to decompose all the ferrous sulphide present, and steam blown through to remove the liberated sulphuretted hydrogen and tarry matter. Excess of dilute sulphuric acid is then added, together with cuprous chloride in an amount equivalent to 2 to 3 per cent. of the total ferrocyanide present, and the whole then distilled in a lead-lined vessel heated with a steam coil. By these means the whole of the cyanogen contents of the ferrocyanide will be distilled off as hydrocyanic acid, which may be absorbed in a solution of caustic soda. The hydrocyanic acid vapour should be first passed through a reflux condenser kept at about 60 to 70° C. to remove the bulk of the water before passing on to

the alkali. The caustic soda solution, when saturated with hydrocyanic acid, may be evaporated under a vacuum to recover the alkaline cyanide.

The liquid left in the still would be a solution of ferrous and ammonium sulphates together with the excess sulphuric acid. On neutralizing the free acid the solution of the two sulphates may be returned to the cyanide scrubber, when the ammonium sulphate will be recovered from the liquid, when the refouled sludge is filter-pressed.

Besides ferrocyanogen compounds, the spent oxide and the cyanogen mud also contain some thiocyanates which accumulate to a considerable degree in the mother liquor after crystallization of the ferrocyanide. As there was but little market for the crude thiocyanate solution, some considerable attention was directed to the possibility of converting it into a more marketable product, such as ferrocyanide or cyanide. One of the earliest processes for its conversion into ferrocyanide was that of A. Gelis,[1] who fused the thoroughly dried thiocyanate with finely divided metallic iron, usually prepared by reduction of the oxide, in a closed vessel to a red heat, but avoiding too high a temperature. The resulting fused mass, like the melt obtained in the old fusion process for the preparation of ferrocyanides from nitrogenous organic matter, contained potassium cyanide and iron sulphide :

$$KCNS + Fe = KCN + FeS,$$

which on solution in water reacted to form ferrocyanide, thus :

$$6KCN + FeS = K_4Fe(CN)_6 + K_2S.$$

Some considerable quantity of ferrocyanide was at one time made by this process, but on a commercial scale it was found more economical to use iron turnings instead of the more expensive reduced iron, the proportion of which was increased to counterbalance the smaller surface exposed. It was also found necessary to keep the air away as much as possible

[1] E.P. 1816 (1860).

from the reacting mass, both during fusion and the subsequent lixiviation to prevent oxidation and consequent loss.

In the subsequent modifications of this process by Gunzburg and Tcherniac[1] the difficulty of drying the thiocyanate was overcome by first fusing the salt at about 300° C., and then grinding it with finely divided iron free from oxide, to obtain a uniform mixture; the product was then heated in a closed vessel to the temperature of boiling sulphur, the vapour of sulphur being used for this purpose. This process was abandoned after being worked for about two years, but was again revived with certain modifications in 1894 by the patents of Hetherington and Muspratt,[2] and Crowther, Rossiter, Hood and Albright,[3] but it is only the latter that shows any advance in this problem, more attention being paid to the drying of the thiocyanate. A current of an indifferent gas was to be passed through the molten mass for some time to remove the trace of water persistently held by the fused salt.

In these processes a conversion of about three-quarters of the total thiocyanate into ferrocyanide takes place, the remaining quarter being left as unaltered thiocyanate.

Goerlich and Wickman[4] proposed that instead of lixiviating the melt resulting from the fusion of the thiocyanate with metallic iron with water, to expose the melt to ordinary air and moisten it with steam, when the following reaction was said to take place :

$$2(6KCN + 6FeS) + 17O + 21H_2O + 2CO_2 = 2K_4Fe(CN)_6 3H_2O + 2K_2CO_3 + 5Fe_2(OH)_6 + 12S,$$

the potassium ferrocyanide and carbonate being recovered by solution in water.

That thiocyanates could be converted into ferrocyanides in aqueous solutions was first shown by

[1] E.P. 1148 (1878); 1359 (1879), and 1261 (1881)
[2] E.P. 5830 (1894). [3] E.P. 8305 (1894).
[4] E.P. 13,264 (9/7/94).

Sternberg,[1] who found that thiocyanates in aqueous solution, when heated with an excess of iron filings and ferrous hydroxide under pressure, were in the greater part converted into ferrocyanides. H. Bower [2] accomplished the same result by heating cuprous thiocyanate with metallic iron, and water under pressure. This result of Bower's work was the outcome of his previous patents,[3] in which he sought to recover the cyanogen compounds from coal-gas ammonia liquor, by first adding an iron salt to convert the cyanide and thiocyanate into ferrocyanide and thiocyanate of iron, and precipitate the two compounds by an acid solution of cuprous chloride after the ammonia had been boiled off with lime. The washed precipitate was treated with finely divided metallic iron which converted the two cyanogen compounds into the corresponding ferrous salts, the insoluble ferrous ferrocyanide being recovered by filtration and converted into an alkali metal ferrocyanide by treatment with a caustic alkali. The filtrate which contained ferrous thiocyanate after evaporation to dryness was added in small quantities at a time to the melt obtained in working the old prussiate process. In his last patent he stated that if the metallic iron is allowed to act on the mixed copper cyanogen compounds at a high temperature and under pressure, that the metallic copper formed in the reaction attacks the thiocyanate, removing the sulphur and forming copper sulphide and ferrocyanide of iron :

$$3Fe''(CNS)_2 + 6Cu_2 = 6Cu_2S + Fe''_2Fe''(CN)_6.$$

In the process of Conroy, Hurter and Brock,[4] finely divided metallic iron is substituted for the more expensive copper of Bower's process, and instead of preparing ferrous thiocyanate, a ferrous (or ferric) salt was added. This process, however, was very similar to that of Sternberg published fourteen years before, the main point of difference being that whereas

[1] D.R.P. 32,892 (1882).
[2] E.P. 361 (3/1/96).
[3] E.P. 8330 and 8381 (1895).
[4] E.P. 3869 (1896).

Sternberg added ferrous hydroxide to facilitate the formation of ferrocyanides, Conroy converted the thiocyanate into the iron salt as in Bower's process by the addition of ferrous salts, and thereby greatly increased the rate of decomposition, a temperature of 135 to 140° C. for five to six hours being sufficient to complete the reaction.

The recovery of the ferrocyanide in marketable form from the insoluble mixture of ferrous ferrocyanide and sulphide was accomplished by the addition of caustic soda. A considerable proportion of the alkali was lost by combination with the ferrous sulphide to form a double iron and alkali metal sulphide, and this fact practically prohibited the use of expensive caustic potash, nor could the alkali metal carbonates be substituted, as the ferrous ferrocyanide was unattacked by these alkalis. This loss of alkali could be overcome by the removal of the ferrous sulphide first, by treatment with dilute hydrochloric acid.

The ferrocyanides of sodium, potassium, iron and calcium are the only representatives met with in commerce. The sodium salt is manufactured chiefly for the production of cyanides, and to a limited extent it is used in the textile industry for colouring and weighting textile fibres and for colouring paper. The potassium salt, although at one time the only raw material for the manufacture of cyanides, is now only used for this purpose to a limited extent, it having been almost entirely displaced by the cheaper and equally efficient sodium ferrocyanide. The principal use of the potassium salt is for the manufacture of the pigment prussian blue. In this respect it has been found impossible to substitute the sodium salt, as the blue made from the latter compound is inferior in colour and in other respects. It is also used for the production of potassium ferricyanide, and here again it has been found impossible to substitute the sodium salt on account of the difficulty of obtaining the sodium ferricyanide in the pure state, due to the

[1] Conroy, *J.S.C.I.*, **17**, 98.

greater solubility and deliquescent nature of the sodium compound.

Both the potassium and sodium ferrocyanides are used in the powdered and anhydrous state as a case-hardening material for steel.

The iron salt is met with in the various shades of prussian blue. The calcium salt has not yet received direct commercial application, but is used solely as a raw material for the production of sodium and potassium ferrocyanides; it is met with in commerce to a limited extent only.

MANUFACTURE OF PRUSSIAN BLUE

The manufacture of this important colouring-matter dates from the discovery by Diesbach in 1704. For many years the details of its preparation were kept secret, and it was not until 1724 that the method became generally known, when Woodward published[1] a process for its manufacture, by first igniting dried blood with potassium carbonate, dissolving the cooled mass in water, adding a solution of ferrous sulphate and alum to the mixture, and then treating the bluish-green precipitate with hydrochloric acid.

In 1754 Macquer showed that the alum had no part in the formation of the colouring-matter and was unnecessary. This addition, however, is still practised to a certain extent at the present day in the manufacture of the cheaper and lighter varieties of the blue for the purposes of adulteration. This investigator also showed that the addition of an alkali to the blue precipitated ferric oxide and generated a soluble salt from which the blue could be again obtained by the addition of iron salts. This soluble salt (potassium ferrocyanide) was obtained in the crystalline form by Sage in 1772. The subsequent discoveries of Scheele, 1782–3, Berthollet, 1790, and Gay Lussac in 1815, added considerably to the knowledge of this colouring-matter and its formation.

[1] *Phil. Trans.*, 1724.

Prussian blue was first manufactured in England at Newcastle in 1770, and was then sold for two guineas a pound. At the beginning of the nineteenth century the price had dropped to about one-quarter of its original, and in 1850 it was sold for 1*s*. 9*d*. per lb.

About the year 1825 potassium ferrocyanide became an article of commerce, and the manufacture of prussian blue increased, but as the preparation of the blue from the ferrocyanide became better understood, finer and purer qualities of the colour were produced. This process never became a simple one, for owing to the extremely fine state of division, and the very colloidal nature of the precipitated blue, the washing was a long and protracted operation which necessitated large tank capacity and floor space; chiefly on account of these facts the industry soon became a very specialized one.

Although prussian blue was made soon after the discovery of Diesbach, yet the industry did not assume any magnitude until potassium ferrocyanide was separated by crystallization from the solution of the melt, obtained by fusing carbonate of potash and animal matter. And the blue was manufactured from this material, instead of from the crude solution of the melt.

As the addition of a solution of a ferric salt to a solution of potassium ferrocyanide resulted in the immediate formation of a blue precipitate, it would seem that this would have been the cheapest and simplest method of preparing the blue. But it was soon found that blues of finer shade and covering power were made, not from the ferrocyanide by direct precipitation with ferric salts, but by precipitation with a ferrous salt, and oxidizing the bluish-white ferrous potassic ferrocyanide with an oxidizing agent.

Amongst the various oxidizing agents used for this purpose may be classed the following:

1. Atmospheric air.
2. Nitric acid.
3. Ferric chloride or sulphate.
4. Chlorine from bleaching powder or nitrohydrochloric acid (aquæ regia).

5. Potassium chlorate and sulphuric or hydrochloric acid.

6. Potassium bichromate and sulphuric acid.

In the first application of the method a dilute but hot solution of potassium ferrocyanide was precipitated with the necessary quantity of ferrous sulphate (copperas) solution, to which a little dilute sulphuric acid had been added to dissolve the basic ferric sulphate usually present in the commercial salt. The bluish-white precipitate of ferrous potassium ferrocyanide was allowed to settle and washed several times by decantation, and finally oxidized by blowing air through it for some time. The blue precipitate was then again well washed by decantation with hot water, filtered on linen filters, and the cake so obtained gently dried at a low heat.

The colouring-matter obtained by this method of oxidation was never very good.

In the more modern methods for the manufacture of the blue, two tanks of about 170 to 200 gallons capacity are placed side by side on a raised platform of sufficient height so that the liquid contents of these tanks could be conveniently run into a third tank placed on the floor level, and the capacity of this bottom tank should be about 800 gallons. Into the two top tanks water is added and well boiled for twenty to thirty minutes to drive off dissolved oxygen as far as possible; and then 180 lb. of commercial ferrous sulphate is added to one, and 200 lb. of potassium ferrocyanide is added to the other, and the liquid contents of each tank is kept boiling and agitated until the salts are dissolved. In the solution of ferrous sulphate a light yellowish-brown precipitate is usually formed of a basic ferric sulphate (sometimes erroneously stated to be ferric oxide) due to the oxidation of some of the ferrous salt and generally present in the commercial article. To prevent the introduction of this compound into the finished blue, about 1 to 2 lb. of sulphuric acid are added, when after a short time the brown precipitate passes into solution as ferric sulphate, and not as is still sometimes stated, as ferrous sulphate.

Steam is then shut off from both tanks, the agitation stopped, and the contents allowed to settle to deposit the mechanical impurities that are generally present in the commercial salts. The ferrous sulphate (copperas) solution is then run into the lower tank and agitated, while the potassium ferrocyanide solution is run slowly in, in a thin stream. When all the liquid has been run into the bottom tank the mixture is stirred for fifteen to twenty minutes, and steam turned on, if necessary, to raise the temperature to about 80° C. The precipitated ferrous ferrocyanide so formed is allowed to settle for from one to two days, and the supernatant liquor decanted off; hot water at a temperature of 60° to 70° C. is then added and the whole well stirred and again allowed to settle and the clear liquor decanted. This washing is repeated until practically the whole of the soluble salts have been removed.

Before oxidation the precipitate must be obtained in as thick a paste as possible, and to accomplish this the excess water must be removed by filtration, by pressure in a wooden press, or by evaporation. The latter is much to be preferred, for although somewhat more expensive it is also more convenient, and prevents a great deal of premature oxidation that would otherwise be unavoidable.

The thick paste, which should be white, but which is usually of a more or less light blue colour, due to some air oxidation which it is practically impossible to avoid, is placed in a tank, preferably fitted with a hood, in a large, well-ventilated room or placed out in the open air. The mixture is thoroughly agitated, and nitric acid added, the agitation being continued, and the blue heated by steam until the temperature rises to 80° to 90° C. Brown fumes of nitrogen oxides are evolved which must not be inhaled, and it is for this reason that the operation should be performed out of doors or under well-ventilated conditions.

After the reaction is over, which is judged by the

fact that brown fumes are no longer evolved, the mixture is heated to boiling and allowed to stand one day and the clear liquor decanted off. The washing is continued with hot water, the mixture being well stirred after each addition of water, until the wash water no longer gives an appreciable precipitate with barium chloride. This washing is an exceedingly troublesome and tedious operation, as the blue settles so slowly, particularly towards the end. The larger the tank capacity, of course, the fewer washes would be required.

After washing, the blue compound is filtered and the cake cut up into cubes of two inches long by one inch thick and dried at a low temperature and finally at 60° to 70° C.

As the oxidation of the white salt by atmospheric air has long since been discarded, so also is oxidation by nitric acid rapidly passing out of use, this method being now little if ever used.

In the oxidation of the ferrous ferrocyanide by ferric salts, ferric sulphate is the usual salt used, and it is made by oxidizing ferrous sulphate solution by the addition of nitric acid and the necessary quantity of sulphuric acid, or by heating ferric oxide or hydroxide with sulphuric acid: the latter method is cheaper and the one generally adopted. The ferric oxide is mixed into a paste with water and the calculated quantity of 70 or 80 per cent. sulphuric acid, and the whole rapidly mixed. The mixture very soon becomes hot and thickens, and finally sets to a white or grey mass containing about 65 per cent. of ferric sulphate. The mass is broken up and dissolved in water; ferric sulphate is very soluble in water though it requires some time to pass into solution.

The solution of ferric sulphate, obtained as above described, is allowed to settle and decanted, or filtered from the insoluble matter and added to the washed ferrous ferrocyanide with agitation. A reaction immediately takes place, the white compound being converted into a blue ferric ferrocyanide, ferrous

sulphate being left in solution. This reaction is usually expressed as follows :

$$2Fe'''_2(SO_4)_3 + 3Fe''K_2Fe(CN)_6 = Fe'''_4[Fe(CN)_6]_3 + 3K_2SO_4 + 3Fe''SO_4.$$

The blue obtained is, however, not pure ferric ferrocyanide as stated above, the reaction being more complicated, the blue containing combined potassium of the composition, $Fe_{11}K_3[Fe(CN)_6]_9 = 3FeKFe(CN)_6 : 2Fe_4[Fe(CN)_6]_3$, and the reaction is more correctly expressed by the following equation :

$$11Fe'''_2(SO_4)_3 + 18Fe''K_2Fe(CN)_6 = 2Fe'''_{11}K_3[Fe(CN)_6]_9 + 15K_2SO_4 + 18Fe''SO_4.$$

This process has the advantage over the preceding methods in that it is not necessary to obtain the ferrous ferrocyanide in the form of a paste, which thus saves the cost of pressing or evaporating the extra water.

The other oxidizing agents are used much in the manner described above, the necessary proportion of oxidizing agent is prepared in solution and added to the ferrous salt, and the blue precipitate washed and dried in the manner described.

Electrolytic oxidation has been advocated in the process of Crowther and Rossiter, in which the ferrous ferrocyanide is suspended in water, strongly acidulated and submitted to electrolysis, oxidation takes place at the anode, and a fine blue with a deep violet reflex obtained.

The blues prepared by the above-described methods differ a little from each other in chemical composition and physical properties. In theory these blues should consist of one definite compound for each particular method used, but in practice the various brands of blue consist principally of one compound containing small quantities of one or more other compounds, due to impurities added with the ingredients or to atmospheric oxidation during the process of manufacture. They are known in commerce under a variety of names, such as china, paris, berlin and prussian blue, etc.

SOLUBLE BLUE (*i.e.* a blue that will form a colloidal solution in water) may be prepared by several methods :

1. By boiling ordinary precipitated prussian blue with a solution of potassium ferrocyanide.

2. By adding a solution of ferrous sulphate or chloride to a solution of potassium ferricyanide insufficient to precipitate all the latter.

3. By adding ferric chloride or sulphate to an excess of potassium ferrocyanide.

When prepared by the latter method 1 cwt. of ferric chloride and 10 lb. of sodium sulphate are dissolved in water, and added to a solution containing 2 cwt. of potassium ferrocyanide. The addition of the sodium sulphate is to render the washing of the blue possible, for although this colouring-matter forms a blue colloidal solution with water, yet it is precipitated by saline solutions. When the blue has settled the clear liquor is decanted and the precipitate thrown on a filter and washed, until the blue begins to pass through the filter into the wash water. This blue in the past enjoyed a wide popularity as a dye, but is now seldom if ever used.

The formation of the compound by the three methods above stated may be expressed by the following equations :

(1) $Fe'''_4[Fe(CN)_6]_3 + K_4Fe(CN)_6 = 4Fe'''KFe(CN)_6$.
(2) $Fe''SO_4 + K_3Fe'''(CN)_6 = Fe'''KFe''(CN)_6 + K_2SO_4$.
(3) $Fe'''_2(SO_4)_3 + 2K_4Fe''(CN)_6 = 2Fe'''KFe''(CN)_6 + 3K_2SO_4$.

By whichever method this blue is prepared it has practically the same composition, and consists essentially of ferric potassium ferrocyanide.

NEUTRAL BLUES are a class of ferric ferrocyanides made by direct precipitation of the ferrocyanide with a ferric salt, but the colours are not so fine as those prepared by the oxidation of the white ferrous compound.

The direct precipitation of a ferricyanide (red prussiate) by a ferrous salt also results in the production of blue compounds of probably similar composition

as that produced from the ferrocyanides by ferric salts, and are often called Turnbull's blue. They are generally produced from the mother liquor obtained in the manufacture of potassium ferricyanides. This salt, which is prepared in solution together with some potassium chloride, is made to yield as much of the ferricyanide as possible by crystallization, and when the potassium chloride becomes too concentrated, the mother liquor is precipitated with ferrous sulphate.

The finer shades of blue are known in commerce as paris blue, china blue and prussian blue, and should consist essentially of an iron cyanogen compound, free from all foreign admixtures, and be prepared by the oxidation of ferrous ferrocyanide precipitated from potassium ferrocyanide solution. Blues of equally fine shade and bronze lustre may be prepared in a similar manner from ammonium ferrocyanide, but the substitution of sodium ferrocyanide yields blues of much lighter shade and with little if any lustre. The addition, however, of potassium or ammonium chloride to the sodium ferrocyanide solution before precipitation with the ferrous salts will on oxidation of the latter yield blues of a shade very similar to those obtained directly from potassium ferrocyanide.

ANTWERP BLUE was a term at one time applied to a light-coloured prussian blue made by adding two parts of ferrous sulphate, one part of zinc sulphate and one part of alum, to a solution of four parts of potassium ferrocyanide, but this product is not on the market at the present time.

BRUNSWICK BLUE was a name applied to a product obtained by precipitating prussian blue in the presence of a large quantity of finely ground gypsum, barytes or china clay, and was made in three shades, pale, medium and deep.

CHAPTER X

MANUFACTURE OF THIOCYANATES AND CYANAMIDE

A GREAT many processes have been proposed and patented for the manufacture of thiocyanates synthetically, and also to recover them from the waste products of the large gas undertakings, several of which have been worked on a large scale, but so far with practically no great commercial profit.

The demand for thiocyanates has in past years been small; a limited quantity was consumed by the textile trade in the form of the tin and aluminium salts as mordants, and a small quantity of the ammonium salt was consumed in photography. At one time also the cuprous salt was used in the manufacture of anti-fouling compositions for ships' bottoms. Of late years a fresh outlet has been found for these compounds in the several processes that have been proposed and worked for their conversion either directly or indirectly into cyanides; with the consequence that some considerable attention has been paid to their manufacture and recovery from the purification products of coal-gas and coke-oven recovery plants.

By the action of ammonium polysulphide or of ammonium sulphide and free sulphur some of the hydrocyanic acid in crude coal-gas is converted into ammonium thiocyanate, which is found in the liquor from the ammonia scrubbers and in the spent oxide of iron.

The liquor obtained from the ammonia scrubber of a gasworks contains, besides a small quantity of am-

monium thiocyanate, a large number of other ammonium compounds, both volatile and fixed. The liquor is first run into a still and distilled without additions, to drive off all volatile ammonium compounds, which consist chiefly of the carbonate and sulphide or hydrosulphide of ammonium, together with a small proportion of cyanide. The correct quantity of milk of lime is then pumped into the still, and the liquor again distilled to drive off the remainder of the ammonia liberated from the fixed ammonium compounds by the added lime.

The residual liquor in the still then contains the whole of the thiocyanate in the form of the calcium salt, together with some calcium sulphate, sulphite, and thiosulphate. Of the many methods proposed, the only practical one for the thiocyanate recovery is to add the requisite quantity of ferrous and cupric sulphates to the neutralized solution, when the thiocyanate is precipitated as the white insoluble cuprous salt, in a very finely divided state. A considerable proportion of sulphate of lime is generally precipitated along with the cuprous salt :

$$Ca(CNS)_2 + 2CuSO_4 + 2FeSO_4 = 2CuCNS + CaSO_4 + Fe_2(SO_4)_3.$$

The mixture is allowed to settle, the clear liquor decanted off, and the solid precipitate filtered by means of a filter-press, or otherwise, and washed. The purified precipitate is converted into the calcium or barium salt by boiling with slaked lime or barium hydroxide and filtered from the cuprous hydroxide. The sodium, potassium or ammonium salt can then be obtained by precipitating the recovered thiocyanate solution with the carbonate of these bases.

This process, with but little modification, was at one time at work in several gasworks in this country. Radcliff [1] proposed to effect some economy in the general method described above, by burning the hydrogen sulphide which passed away with the waste

[1] E.P. 10,075 (13/5/05).

gases from the ammonium sulphate plant, and to absorb the sulphur dioxide so formed in water, or some waste liquor from the ammonia stills, and to use this weak sulphurous acid in place of the ferrous sulphate solution to reduce the copper in the precipitation of the thiocyanate.

When the crude cuprous thiocyanate was treated with lime for the recovery of the thiocyanate, the copper was left behind as cuprous hydroxide, generally contaminated with some sulphate of lime. The copper could be recovered by digesting it with dilute sulphuric acid in which a quantity of sodium chloride had been dissolved, thus :

$$Cu_2O + H_2SO_4 + 4NaCl = Na_2SO_4 + 2NaCu'Cl_2 + H_2O.$$

or by a dilute solution of hydrochloric acid. If, however, dilute sulphuric acid alone were used, only half of the copper would be recovered in solution as cupric sulphate, the remainder being left behind as metallic copper :

$$Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O.$$

The solution of sodium cuprous chloride may be used for precipitating the thiocyanate from a fresh quantity of crude liquor, and if kept from oxidation it would not require the addition of reducing agents.

This method was but little practised, and at the present day is practically abandoned, for, owing to the low price of thiocyanates, the process would not bear the cost of the recovery, nor the use and loss of such an expensive material as copper sulphate.

Thiocyanate in the form of the ammonium salt is a constituent of spent oxide of iron, the material which has been used for arresting the hydrogen sulphide in the purification of coal-gas. This material contains besides sulphur and tar some insoluble ferrocyanides, ammonium sulphate and thiocyanate. The amount of this latter body varies in different spent oxides from a trace up to 2 or 3 per cent., and in some cases as much as 5 or 6 per cent.

As the thiocyanate is formed in the spent oxide by the reaction :

$$2(NH_4)HS + S_2 + 2HCN = 2NH_4CNS + 2H_2S,$$

the amount existing in the spent oxide depends directly on the efficiency of the ammonia scrubbers, which should remove the bulk of the ammonium compounds out of the gas before it enters the oxide purifying boxes.

The thiocyanates could be readily extracted from the spent oxide by placing the material in tanks fitted with false bottoms, and systematically leached with water and weak solutions, and the liquor after distilling off the ammonia with slaked lime, precipitated with copper and ferrous sulphate.

This method was practised, but the handling of so large a bulk of material for a small percentage of product did not pay while the price of thiocyanates was low, and again, the percentage of sulphur was reduced by the water in the residual spent oxide, and it needed drying before it could be sold for its sulphur contents to the sulphuric acid manufacturers.

In the works where ferrocyanides are extracted from the spent oxide, an accumulation of sodium thiocyanate occurs in the mother liquor after the bulk of the ferrocyanide has crystallized out.

This thiocyanate was derived partly from the ammonium thiocyanate originally existing in the spent oxide and partly formed by the decomposition of some of the ferrocyanide, by polysulphide during the course of the extraction, and also by decomposition of the so-called " non-blueing " cyanogen compounds, which exist in most spent oxides, into thiocyanate, by the combined action of the sulphur and the alkali.

This mother liquor, if consisting of sodium salts, when evaporated so that the sodium thiocyanate contents was equal to 10 to 12 per cent. and then left to cool, practically the whole of the ferrocyanide in the liquor was deposited in the form of crystals ;

sodium ferrocyanide being almost insoluble in a cold 10 per cent. solution of sodium thiocyanate. The liquor from these crystals, if further evaporated to a strength of 18 to 20 per cent. sodium thiocyanate, became in recent years a marketable article for conversion into cyanide, by one or other of the various processes that have been tried commercially for making cyanides from thiocyanates.

Increased yields of thiocyanates may be obtained by digesting the spent oxide under a steam pressure of about 30 lb. per square inch with an excess of slaked lime, and agitating the mixture. After about three-quarters to one hour the whole of the cyanogen compounds in the spent oxide are converted into the one form of thiocyanates. The total thiocyanate formed, however, usually exceeds the sum of the amount originally present in the spent oxide, and the theoretical amount due to the conversion of the ferrocyanides by as much as 2 to 3 per cent.; sometimes as much as 4 or 5 per cent. has been found.

This excess thiocyanate is due to the fact that has long been recognized, that spent oxide frequently contains cyanogen compounds other than ferrocyanides, and thiocyanates, generally known as non-blueing cyanogen compounds, which under the treatment above described are converted quantitatively into thiocyanates.[1]

Owing to the greater ease with which the hydrocyanic acid existing in the crude coal-gas can be recovered in the form of thiocyanate, and to the advance made in recent years in the conversion of thiocyanates both directly and indirectly into cyanides, the tendency with the modern gas undertakings is to scrub the gas in such a manner as to convert the hydrocyanic acid wholly into thiocyanates, and to avoid the formation of complex ferrocyanides.

Among the earlier processes for this purpose various

[1] H. E. Williams, *J.S.C.I.*, 31, 315.

alkalis were employed in conjunction with sulphur,[1] such as caustic soda, magnesia, lime, etc.

The mixture of alkali and sulphur was first placed in specially designed scrubbers in contact with the crude coal-gas before it entered the ammonia scrubbers; the hydrogen sulphide in the crude gas combined with the alkali to form sulphide, which then dissolved sulphur with formation of polysulphide:

$$(1)\ NaOH + H_2S = NaHS + H_2O.$$
$$(2)\ 2NaHS + S_4 \rightleftarrows Na_2S_5 + H_2S.$$

The reaction expressed above is a reversible one, hydrogen sulphide attacking the newly formed polysulphide precipitating sulphur. Under the conditions present in the gas scrubber, *i.e.* the presence of an excess of both sulphur and hydrogen sulphide, about 50 per cent. of the alkaline sulphide was in the form of polysulphide. This was a disadvantage, as only the polysulphide reacted in the formation of thiocyanates, thus:

$$Na_2S_5 + 2HCN = 2NaCNS + S_3 + H_2S.$$

These processes, which were all the same in chemical principle, the difference being merely in the particular alkali used, were generally worked in two stages. The crude gas was first passed through some previously made polysulphide solution whereby the hydrocyanic acid was removed, and then on into another vessel into which some alkali and sulphur had been placed suspended in water, and polysulphide formed ready for a fresh change in the cyanide scrubber.

Some considerable difficulty was encountered in the formation of the polysulphide, owing to the tar introduced by the crude gas coating the surface of the sulphur, and preventing contact with the alkaline sulphide, the sulphur being frequently cemented together in large masses.

This process was considerably improved upon by using the ammonia in the gas as the alkali. Some

[1] J. Tcherniac, E.P. 24,767 (11/11/02); 2708 (3/2/06). C. C. Carpenter, E.P. 22,710 (18/10/02); 8166 (8/4/03), etc.

sulphur and water were introduced into one bay of the cyanide scrubber and the crude gas passed through ; ammonia and hydrogen sulphide were absorbed by the liquid, and the so formed ammonium sulphide rapidly dissolved sulphur to form polysulphide. When the solution became sufficiently strong it was allowed to flow into a second bay to absorb the hydrocyanic acid. This process had the advantage over those previously described in that no alkali was used other than that existing in the gas, and also that the ammonium polysulphide was not precipitated by hydrogen sulphide, the reaction :

$$2NH_4HS + S_4 = (NH_4)_2S_5 + H_2S$$

not being a reversible one. And again the finished liquor could be easily freed from excess sulphides by simply boiling the liquor.

An ingenious modification of the ammonium polysulphide process has been worked out by P. E. Williams[1] in which both the polysulphide and ammonium thiocyanate are made in the same apparatus, the two reactions proceeding simultaneously. The gas is allowed to pass through a layer of spent oxide about 14 in. thick, which is kept in a moist state by occasionally spraying with water. The hydrogen sulphide and ammonia in the gas unite in the presence of water to form ammonium sulphide which immediately dissolves some of the sulphur of the spent oxide to form polysulphide. The whole surface of the spent oxide is thus covered with a film of ammonium polysulphide solution, forming thereby a most perfect and efficient cyanogen scrubber, the hydrocyanic acid combining directly with the polysulphide to form the thiocyanate.

At intervals of about twenty-four hours, the oxide in the box is sprayed with water or weak liquor, and the solution of the ammonium thiocyanate displaced by the fresh liquor run off.

The finished liquor so obtained is first boiled to

[1] E.P. 23,604 (1909).

remove volatile ammonium salts, then again boiled with lime to drive off all combined ammonia and to obtain a solution of about 20 per cent. strength of calcium thiocyanate.

If the liquor obtained in the first operation is not sufficiently strong in thiocyanates it is used again for spraying the oxide.

Of the synthetical methods for the manufacture of thiocyanates, the simple method of Gelis [1] is the best known, and probably the only one worked on a practical scale.

Ammonium sulphide and carbon disulphide were placed in a closed vessel fitted with an agitator, and reaction took place with formation of ammonium thiocarbonate :

$$(NH_4)_2S + CS_2 = (NH_4)_2CS_3.$$

Potassium sulphide was then added and the mixture heated under pressure, and potassium thiocyanate formed thus :

$$2(NH_4)_2CS_3 + K_2S = 2KCNS + 2(NH_4)HS + 3H_2S.$$

The evolution of so large a quantity of hydrogen sulphide was a great drawback and difficulty of this process, and the efforts of later investigators were all directed towards the removal of this difficulty, and to the reduction of the ammonia necessary.

In the process of Gunzburg and Tcherniac [2] ammonia was substituted for the ammonium sulphide. Ammonia and carbon disulphide were heated to 100° C. in a closed vessel and agitated, ammonium thiocyanate being formed by the reaction :

$$CS_2 + 4NH_3 = NH_4CNS + (NH_4)_2S.$$

Considerable pressure arose in the vessel owing to the evolution of ammonium sulphide.

This process, though a considerable improvement on the original in that it prevented the formation of hydrogen sulphide, still required the use of a very large quantity of ammonia, only one-quarter of which

[1] E.P. 1816 (1860). [2] E.P. 1148 (1878) and 1261 (1881).

was converted into thiocyanate while one-half was formed into ammonium sulphide.

The difficulty in the use of a large excess of ammonia was overcome in a somewhat simple manner by the process of H. W. Crowther and Rossiter,[1] in which lime was used.

The ammonia solution together with the carbon disulphide and lime is placed in an autoclave fitted with stirrers and heated with steam until the pressure rises to about 20 lb.; the heating is then discontinued, although the pressure rises considerably higher.

When the reaction:

$$2NH_3 + 2CS_2 + 2Ca(OH)_2 = Ca(CNS)_2 + Ca(HS)_2 + 4H_2O$$

is complete, the excess of ammonia which was generally used is distilled off, and carbon dioxide passed through the solution to decompose the calcium sulphydrate, and filtered from the precipitated carbonate of lime.

The removal of the excess sulphur was proposed by E. Beringer[2] by the use of a zinc salt: 230 lb. of crystallized zinc sulphate was to be mixed together with 90 gal. of water and 230 lb. of ammonia solution (Sp. Gr. 0.91), and the whole added to 60 lb. of carbon disulphide in a closed vessel and heated to 100° C. It was proposed to use the zinc sulphide formed as a substitute for white lead.

The addition of an oxidizing agent was proposed by J. J. Hood and A. G. Salaman.[3] The ammonia and carbon disulphide were to be heated with Weldon mud or ferric hydroxide such as bog ore in a closed vessel to 100° C. or higher.

The use of nitrogen in the form of a nitrite in place of the ammonia was the subject of a patent.[4] Potassium nitrite and carbon disulphide were to be heated together in a closed vessel to about 120° C., and hydrogen sulphide then pumped in:

$$KNO_2 + CS_2 + 2H_2S = KCNS + S_3 + 2H_2O.$$

[1] E.P. 17,846 (22/9/93) and 21,451 (1893).
[2] E.P. 11,108 (19/6/00).
[3] E.P. 5351 (25/3/91).
[4] E.P. 11,287 (3/6/95).

CALCIUM CYANAMIDE

Calcium cyanamide is at the present time a product of considerable industrial importance, and the process which resulted in its commercial production was the outcome of the researches of Prof. Frank and Dr. N. Caro on the cheap production of cyanides.[1] It is chiefly manufactured for application to the soil as an artificial nitrogenous fertilizer, and for the manufacture of ammonium sulphate and other nitrogen compounds.

Calcium carbide, prepared by heating lime and coke in an electric furnace to a very high temperature :

$$CaO + 3C = CaC_2 + CO$$

is finely ground and placed in specially designed cylinders, which are electrically heated from the inside to about 1000° C. ; at one end of the cylinder pure nitrogen is passed over and rapidly absorbed :

$$CaC_2 + N_2 = CaCN_2 + C.$$

The combination of the carbide with the nitrogen is an exothermic reaction, and after a certain portion of the nitrogen has been absorbed sufficient heat is liberated to maintain the reaction temperature, independent of any external source of heat, which at this stage may be cut off. The temperature must not be allowed to run too high, due to a too rapid absorption of nitrogen, or a reversal of the above reaction may set in, as well as other secondary reactions, with destruction of some of the freshly formed cyanamide. The complete conversion of one charge of carbide into cyanamide takes from thirty to forty hours.

When the nitrogen has ceased to be absorbed, the resulting product, which has caked to a clinker-like mass resembling coke, is cooled and ground to an exceedingly fine powder, and it is placed on the market packed in sheet-iron drums or in double bags lined with paper. In its finished condition it contains

[1] E.P. 25,475 (2/12/98).

19 to 20 per cent. of nitrogen, 2 per cent. or under of unaltered calcium carbide and much free lime, and if required for agricultural purposes it is usually mixed with 2 per cent. of oil.

The nitrogen required for the process, which must be especially pure and free from oxygen, is usually made by the Linde process [1] from the atmosphere. In this process, by liquefying and fractionally distilling atmospheric air, nitrogen may be obtained of 99 to 99.5 per cent. purity. This is the process most generally adopted for the separation of the nitrogen necessary for the manufacture of calcium cyanamide. As, however, the apparatus necessary for the preparation of nitrogen by this method is very costly, and involves a large capital outlay; and also as has been shown in recent years, explosions are liable to occur, the cause or causes of which are at present unexplained; which may completely wreck the plant, some attention has been devoted to the production of nitrogen by other means.

These processes are practically confined to the deoxidation of atmospheric air, and may be classed under two heads:

1. Deoxidation of the air by an agent, the oxidation product of which is non-volatile.

2. Deoxidation of the air by an agent the oxidation product of which is volatile.

In the first case air is passed over heated copper turnings, whereby the oxygen is absorbed by the copper with formation of oxide and leaving the nitrogen. The copper when oxidized may be reduced and made active again by passing combustible gases over the heated oxide.

This process, which has been worked commercially, particularly in America, works rapidly and well at first, but the removal of the last few per cent. of oxygen has proved a considerable difficulty, probably due to the large dilution with the nitrogen which prevents the oxygen coming in contact with the copper.

[1] E.P. 14,111 (1902); *see also* Linde, 12,528 (1895).

In the second case air is passed over heated carbon or sulphur and the oxidation products scrubbed out of the resulting gas by suitable means. The gases obtained by the action of carbon or coke would consist essentially of carbon dioxide and nitrogen ; the former gas could be removed by absorption in a solution of sodium carbonate or milk of lime, or it could also be easily separated by compression ; the great difficulty, however, would be the impossibility of exactly regulating the combustion of the carbon, as the gas would either contain some small quantity of oxygen in excess or some carbon monoxide, either of which in small quantities would be exceedingly difficult to eliminate for the reason already explained.

With sulphur the difficulties experienced above could be practically avoided, for if air were passed over heated sulphur, the latter in excess, the resulting gases would consist of nitrogen and sulphur dioxide with a little sulphur vapour, but would be almost oxygen free ; the sulphur dioxide might be readily removed by scrubbing with milk of lime. In this case, however, the materials used are more expensive.

Calcium cyanamide in the moist state slowly decomposes, the nitrogen passing into ammonia, and it is to this reaction that the value of this product as a fertilizer is due. The liberated ammonia is oxidized, by the nitrifying organisms of the soil, into nitric acid, the form in which nitrogen is assimilated by plants.

This decomposition into ammonia can be greatly accelerated by heating the cyanamide under pressure with superheated steam, when in a short time the whole of the nitrogen is converted into ammonia, the pressure in the converter rising considerably :

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3.$$

This reaction is being used on a large scale for the production of ammonium sulphate, by passing the liberated ammonia into sulphuric acid. And also for the manufacture of nitric acid of high strength, by passing the ammonia vapour mixed with the requisite

quantity of air over a specially prepared platinum catalyzer at a high speed according to the patent process of Prof. Ostwald. If some of the ammonia is allowed to by-pass the catalyzer, and ultimately mix with the nitric acid, ammonium nitrate may be obtained.

By treating the crude product with water, a solution of calcium cyanamide is obtained which on boiling is decomposed into calcium hydroxide and cyanamide; and this latter body rapidly polymerizes to form dicyandiamide (cyanoguanidine):

(1) $CaCN_2 + 2H_2O = Ca(OH)_2 + CN_2H_2$
(2) $2CN_2H_2 = C_2N_4H_4$,

the latter compound crystallizing out on cooling the filtered solution. Dicyandiamide is used in the synthetic dye industry, and as the nitro compound in the manufacture of explosives.

By suitable treatment with acids, calcium cyanamide can be made to yield up its nitrogen in the form of urea; a product that has in recent times found application in applied synthetical chemistry:

$$CaCN_2 + 2H_2O = (NH_2)_2CO + CaO.$$

When fused with sodium chloride under suitable conditions, it has been claimed that a quantitative yield of cyanide may be obtained.

Guanidine salts can also be produced by heating the corresponding ammonium salts with the purified dicyandiamide or melamine.

Thus this substance, besides finding application as an artificial manure, may be used for the economical production of ammonium salts, nitric acid, dicyandiamide, urea, as a raw material for the production of cyanide, and has also found application under the name of "Ferro-dur" as a case-hardener for iron.

CHAPTER XI

MANUFACTURE OF CYANIDES FROM FERROCYANIDES AND THIOCYANATES

In the earlier attempts for the production of cyanides, potassium ferrocyanide was the only source of raw material, and the cyanide was produced by the method first proposed by Berzelius, which consisted in fusing the carefully dried product in a crucible out of air contact, when potassium cyanide and iron carbide were formed, and free nitrogen evolved :

$$K_4Fe(CN)_6 = 4KCN + Fe + C_2 + N_2.$$

The molten mass was poured out into cakes which were broken up when cold; but little attempt was made to purify the product, which was very dark-coloured, from the insoluble contents of iron carbide and free carbon, and it was put on the market in this form.

This process not only resulted in a black-looking mass, but was very wasteful, as one-third of the total cyanogen contents of the ferrocyanide was destroyed. In order to overcome this loss the anhydrous ferrocyanide was fused with dry carbonate of potassium : [1]

$$K_4Fe(CN)_6 + K_2CO_3 = 5KCN + KCNO + CO_2 + Fe,$$

whereby a more economical yield of cyanide was obtained, only one-sixth of the theoretical being lost, and moreover as the molten cyanide could be decanted from the metallic iron, a much purer product and of better appearance was obtained, contaminated only

[1] F. E. Rodgers, *Phil. Mag.* (1834) [3], 4, 93.

with the potassium cyanate and the excess potassium carbonate. Chiefly on account of its lower price sodium carbonate was later substituted for the potassium carbonate with equal success, but the actual cyanogen contents were higher than if potassium carbonate were used, due to the lower combining weight of sodium.

Various attempts were made to recover some of the cyanogen combined as cyanate, by converting that body into the marketable cyanide, with but little success, and any conversion that was made was more than counterbalanced by the increased cost of production. Adler [1] proposed the addition of more dry ferrocyanide to the melt obtained after fusion with potassium carbonate. In the process of Etard the anhydrous ferrocyanides were to be fused with thiocyanates, and the evolved cyanogen absorbed in caustic soda solution :

$$K_4Fe(CN)_6 + KCNS = 5KCN + FeS + (CN)_2,$$

or with the addition of potassium carbonate to the mixture before fusion in order to avoid the production of cyanogen, thus :

$$K_4Fe(CN)_6 + KCNS + K_2CO_3 = 6KCN + FeS + KCNO + CO_2.$$

Dalinot claimed a higher yield of potassium cyanide by fusing the anhydrous ferrocyanide with dry sodium or potassium hydroxide, and finely powdered calcium carbide :

$$K_4Fe(CN)_6 + 2NaOH + CaC_2 = 4KCN + 2NaCN + CaO + Fe + C_2 + H_2O.$$

The mass was to be stirred during fusion and finally filtered through a hot filter in the molten state.

Better yields of cyanide by the reduction of the cyanate were claimed by J. E. Chester,[2] who proposed to grind the anhydrous ferrocyanide with a mixture of the hydroxide, or carbonate of an alkali, or alkaline earth metal, and 5 per cent. of carbon together with

[1] E.P. 13,531 (July 1900).
[2] E.P. 15,941 (21/8/94).

sufficient tar or pitch to make a pasty mass, and to then fuse the mixture in a furnace.

E. Erlenmeyer [1] in a very simple manner entirely avoided the formation of cyanate, or the loss of any of the cyanogen contents of the ferrocyanide, and also obtained a product of great purity by fusing the carefully dried ferrocyanide with metallic sodium out of air contact :

$$K_4Fe(CN)_6 + 2Na = 4KCN + 2NaCN + Fe.$$

The molten cyanide was poured off the spongy metallic iron into moulds, and obtained in white crystalline blocks in quantitative yield. This beautifully simple process was for many years but little used, chiefly on account of the high price, and the limited production of metallic sodium; and it was some fourteen or fifteen years after Erlenmeyer's discovery before the process was first applied on a manufacturing scale in Germany. The commercial application of the process was, of course, directly due to the fact that it had been made possible to produce metallic sodium by cheaper and more efficient means.

The product obtained by this process consisted of a fused crystalline mass of porcelain-like whiteness, and vastly superior in appearance to the product obtained by the older processes mentioned above; it was composed of a mixture of sodium and potassium cyanide. As the cyanogen contents of sodium cyanide is much greater than that of the potassium salt, the cyanogen of the pure melt, if calculated as potassium cyanide, would yield a figure above 100 per cent., and it was customary in the early application of this process to bring the cyanide contents down to equal 98 to 100 per cent. calculated as potassium cyanide. This reduction in strength was accomplished by adding a weaker cyanide melt obtained by fusing the spongy iron obtained in the first operation, with sodium carbonate. Thus a fused cyanide made by this process and containing cyanogen equivalent to 100 per

[1] *Ber.* (1876), **9**, 1840.

cent. potassium cyanide would contain a considerable proportion of other salts, which was usually carbonate of sodium, for example :

POTASSIUM CYANIDE, 98 TO 100 PER CENT.

Actual Contents		*Calculated Contents*	
Potassium cyanide	66.7	As potassium cyanide	66.7
Sodium cyanide	25.1	Sodium cyanide calculated	
Sodium carbonate	8.2	as potassium cyanide	33.3
	100.0		100.0

About the year 1900 some ten years after the commercial application of Erlenmeyer's process, sodium ferrocyanide was being produced in large quantities ; and from that time on it has gradually displaced potassium ferrocyanide from the market as a raw material for the manufacture of cyanides. At first a mixture of anhydrous sodium and potassium ferrocyanide was used, and the cyanogen contents of the melt brought down to the basis of 100 per cent. calculated as potassium cyanide by the addition of a weak cyanide melt obtained as above described, and in this case, of course, a much larger contents of sodium carbonate could be introduced, without the potassium cyanide equivalent dropping below the 100 per cent.

As high strength sodium cyanide was made in large quantities by synthetical methods, and found to be as equally efficient as the potassium cyanide for the purpose of extracting gold from its ores, the demand for pure sodium cyanide by the cyanide consumers increased, and sodium ferrocyanide almost entirely replaced the potassium salt for the production of cyanides by this process. This resulted in the production of a sodium cyanide of remarkable commercial purity of from 128 to 131 per cent. calculated as potassium cyanide.

Although at the present time sodium cyanide has almost entirely replaced the potassium salt, the unit still remains on the potassium basis.

The metallic iron which was thrown out of combination with the ferrocyanide by the metallic sodium, was either hydraulically pressed in the heated and spongy state, or rendered more fluid by the addition of lead alloyed with the sodium in the preliminary fusion.[1]

The sodium lead alloy was fused in an iron pot under a small quantity of sodium cyanide manufactured in a previous operation and the anhydrous ferrocyanide gradually added. When the operation was complete, the fused cyanide was poured off the top, leaving the reduced iron, containing a little lead, floating on the bulk of the molten lead. Both these methods were used on a manufacturing scale, but at the present day, though but comparatively little cyanide is made from ferrocyanide, the former method, that of hydraulically pressing the iron, is generally adopted.

Metallic zinc has been proposed as a substitute for the metallic sodium.[2] The dried ferrocyanide was to be fused with zinc with formation of a double zinc cyanide, and the zinc subsequently removed by the addition of sodium carbonate or sulphide to the fused mass, and the cyanide separated from the precipitated zinc by decantation or by solution in water.

Although the only methods of making cyanide from ferrocyanide that were successful on a commercial scale were the fusion processes above described, yet great efforts were made to obtain the cyanide in the wet way, by distilling the ferrocyanide with an acid, and absorbing the evolved hydrocyanic acid in a caustic alkaline solution, from which the solid cyanide could be recovered by evaporation.

This apparently simple process was found in practice to be particularly difficult, and the reason of this difficulty arose from two causes : first the difficulty of

[1] Goerlich and Wichmann, E.P. 8889 (4/5/94); A. E. Hetherington and F. Hurter, E. K. Muspratt, E.P. 5832 (28/3/94); *J.S.C.I.*, 14, 271.

[2] H. W. Crowther, E. C. Rossiter and G. S. Albright, E.P. 9275 (10/5/94).

recovering the cyanide from the aqueous solution in a marketable state, and without loss; and secondly that when an alkali metal ferrocyanide is distilled with a dilute mineral acid, only 50 per cent. of the total cyanogen is evolved as hydrocyanic acid, the remainder being precipitated as the insoluble ferrous potassic (or sodic, etc.) ferrocyanide. The ferrous salt formed by the decomposition of 1 molecule of ferrocyanide precipitates an equivalent quantity of unaltered ferrocyanide. This reaction may be expressed:

$$2K_4Fe(CN)_6 + 3H_2SO_4 = 6HCN + 3K_2SO_4 + Fe''K_2Fe(CN)_6$$

and proceeds at a very rapid rate, the hydrocyanic acid being abundantly evolved; only the theoretical acid stated in the above equation is necessary, and sodium or potassium bisulphate or certain organic acids such as tartaric or oxalic acid will act in a similar way.

When the above reaction has gone to completion and the distillation continued with the addition of more dilute mineral acid, only traces of hydrocyanic acid are evolved, the insoluble double ferrous salt decomposing in an exceedingly slow manner. By increasing the strength of the acid this slow rate of decomposition may be slightly increased; when distilled with a 30 per cent. solution of sulphuric acid, the insoluble compound can with difficulty be decomposed after boiling for a considerable time. Any of the ferrous ferrocyanide, however, that has been allowed to oxidize to prussian blue will remain in the still undecomposed.

This method of decomposing ferrocyanides is quite impracticable commercially, as the very large excess of acid required would be much too costly and the time taken for the distilling operation much too long. Moreover, owing to the high strength of the acid, quite a considerable loss would occur at the temperature of distillation, due to hydrolysis of the liberated hydrocyanic acid:

$$HCN + 2H_2O = NH_3 + HCHO_2.$$

In order to overcome this difficulty in the decomposition of alkali metal ferrocyanides, a variety of schemes was devised. In most of these it was proposed to distil the ferrocyanide with the calculated amount of acid, and to recover half of the hydrocyanic acid, which may be obtained easily and rapidly, and reconvert the insoluble ferrocyanide into sodium or potassium ferrocyanide. Treatment with sodium or potassium carbonate proved quite unsuccessful, as these alkalis had practically no action on the double ferrous ferrocyanides even on boiling, but they were completely decomposed by solutions of the caustic alkalis if the latter were in sufficient excess.

In the patents of Grossmann[1] it was proposed to distil the ferrocyanide with the theoretical amount of sulphuric acid to decompose half the ferrocyanide, and to recover the insoluble ferrous ferrocyanide by treatment with an excess of a ferric salt solution, thus :

$$3Fe''K_2Fe(CN)_6 + 4FeCl_3 = Fe_4[Fe(CN)_6]_3 + 3FeCl_2 + 6KCl.$$

The reaction was not quite so simple as that expressed above, the blue obtained being not pure ferric ferrocyanide but a ferric potassium salt. The blue formed by this reaction was to be filtered off, and converted into a soluble ferrocyanide by boiling with a caustic alkali. In the patent of 13/6/03, he proposed to add the necessary quantity of caustic soda solution to the insoluble ferrous ferrocyanide and to complete the decomposition by blowing air through the mixture. The solution of the ferrocyanide, separated from the black ferrosoferric oxide by filtration was enriched with more ferrocyanide and distilled with the calculated quantity of acid in the manner described above, thus forming a cycle of operations whereby the whole of the ferrocyanide could be ultimately decomposed by distillation with sulphuric acid.

The difficulty of recovering the cyanogen from the insoluble ferrous ferrocyanide was overcome by the

[1] Grossmann's Cyanide Patent Syndicate, E.P. 4513 (1903).

patent of W. E. Sims and H. Bowes [1] in a simple and ingenious manner, but could only be applied in conjunction with the cyanogen recovery process of a gasworks. These inventors, after decomposing 50 per cent. of the ferrocyanide by an acid distillation, separated the free acid and soluble salts from the insoluble ferrocyanide as much as possible, and added an excess of alkaline carbonate with, if necessary, some ferrous hydroxide, placed the mixture in the cyanogen scrubber of a gasworks' purification plant, and passed a stream of impure coal-gas through it, whereby a large portion of the insoluble ferrocyanide passed into solution. The basic ferrous iron of the ferrocyanide combined with the hydrocyanic acid of the gas to form sodium ferrocyanide, which was recovered in the usual manner. Unfortunately for the success of this operation it was practically impossible by this means to obtain all the ferrocyanide in solution, a part was always in solution, and the remainder was left in the sludge in an insoluble form.

By substituting the ferrocyanides of ammonium or magnesium for the potassium or sodium salt, or any of the sparingly soluble double salts containing these metals, in the distillation with acid the reaction proceeds in an exactly similar manner, only half of the total cyanogen is readily evolved as hydrocyanic acid, the remainder being fixed as the double ferrous ferrocyanide.

The ferrocyanides of the alkaline earth metals, including the lithium and hydrogen salts, when boiled in solution with dilute acids decompose in a somewhat more simple manner, as two-thirds of the total cyanogen is evolved as hydrocyanic acid, the remaining third being fixed as the pure ferrous ferrocyanide, $Fe''_2Fe(CN)_6$, as these bases do not appear to form double ferrous salts.

The distillation of calcium ferrocyanide with an acid was the subject of a patent taken out by J. H. Paul,[2] in which a solution of calcium ferrocyanide was

[1] E.P. 2929 (7/2/06). [2] E.P. 72 (January 1903).

to be distilled with dilute sulphuric acid in sufficient excess to maintain 10 to 20 per cent. of free acid in solution. It was claimed by the inventor that all the ferrocyanide was decomposed in this way. Two-thirds of the hydrocyanic acid was, of course, readily obtained according to the reaction explained above :

$$3Ca_2Fe(CN)_6 + 6H_2SO_4 = 12HCN + Fe''_2Fe(CN)_6 + 6CaSO_4,$$

but the remainder was obtained only with great difficulty, by continuous and prolonged boiling. The ferrous ferrocyanide that is precipitated after the reaction expressed above is complete, certainly decomposed at a somewhat greater rate than the double ferrous ferrocyanides, but the time taken is much too long, and also any oxidation of the ferrous salt that takes place, or any alkali metal that may be introduced with the water or any of the ingredients will render a portion of the insoluble matter unattacked by the acid. Some of the hydrocyanic acid would also be probably lost owing to hydrolysis by prolonged contact with the strong acid solution.

A better method than the above for the decomposition of calcium ferrocyanide would be to distil the solution with the exact acid theoretically necessary to decompose the two-thirds of the ferrocyanide into hydrocyanic acid. If when this reaction is complete milk of lime is run into the boiling but practically neutral liquor, the whole of the ferrous ferrocyanide, unlike the corresponding double alkali metal ferrocyanide, is instantly and completely decomposed :

$$Fe''_2Fe(CN)_6 + 2CaO = Ca_2Fe(CN)_6 + 2FeO.$$

The calcium ferrocyanide solution recovered by filtration is enriched with more ferrocyanide and redistilled with the necessary acid. Thus, if sufficient calcium ferrocyanide were available, the chief difficulty attending the decomposition of alkali metal ferrocyanides by acids is surmounted without recourse to the loss and expense of prolonged distillation operations, or a series of tedious recovery processes.

When a solution of a ferrocyanide is boiled in a neutral solution with sufficient mercuric chloride, the whole of the cyanogen contents of the ferrocyanide is converted into mercuric cyanide, from which the cyanogen may be recovered as hydrocyanic acid, by distilling it with a suitable acid. In this process, which has been worked out by Feld,[1] mercuric chloride is added to the ferrocyanide which, if alkaline, should be previously treated with salts, of which the hydroxide, carbonate, or oxide is not able to separate insoluble mercuric compounds from the mercuric chloride solution, such, for example, as the chloride of magnesium. Sufficient mercuric chloride should, of course, be added to convert the whole of the cyanogen of the ferrocyanide into mercuric cyanide thus :

$$Na_4Fe(CN)_6 + 3HgCl_2 = 3Hg(CN)_2 + FeCl_2 + 4NaCl,$$

and the mixture boiled for some time. When this operation is complete, and all the cyanogen is combined as mercuric cyanide, dilute sulphuric acid is added and the mixture carefully distilled until the whole of the mercuric cyanide is decomposed into hydrocyanic acid, and the latter absorbed in caustic soda solution, from which the sodium cyanide is recovered by careful evaporation.

The residual liquor left in the still after all the hydrocyanic acid has been distilled off is regenerated with an oxidizing substance, and the so-treated liquor, after removal of the iron salt formed by the decomposition of the ferrocyanide, may be used for converting more ferrocyanide into mercuric cyanide.

Dilute sulphuric acid will not decompose mercuric cyanide completely, and it is necessary that some hydrochloric acid or chloride be added. In the method above described ample chloride exists in the solution for this purpose.

The chief commercial difficulty of the process is that it is necessary to add the theoretical quantity of mercuric chloride to combine with all the cyanogen of

[1] E.P. 24,920 6/12/01 ; G.P. 141,024 (13/10/01).

the ferrocyanide to form mercuric cyanide, and thus a large amount of expensive material is involved in the operation. Again, the recovery of the mercuric salt remaining in solution after the decomposition of the mercuric cyanide is by no means a particularly easy or simple operation, and offers practically no saving in time or labour over the method of recovering the ferrocyanide from the insoluble ferrous ferrocyanide obtained in the simple distillation process; the latter of which does not require the use of other expensive material.

The salts of mercury and silver were at one time thought to be the only metallic bases capable of displacing the iron from a ferrocyanide in aqueous solutions. This, however, is not so;[1] cuprous chloride and cuprous oxide, or hydroxide, also decompose a ferrocyanide, and the latter when boiled with an alkaline solution of a ferrocyanide in contact with the air, forms a double cuprocyanide and a precipitate of ferric hydroxide. This reaction has been worked out on a manufacturing scale[2] as a process for obtaining cyanides from ferrocyanides by distillation with an acid, and offers several important advantages over those previously described, in that no preliminary treatment whatever is required, and only a very small proportion of the cuprous salt is necessary, the decomposition of the ferrocyanide proceeding smoothly to completion.

To the ferrocyanide in solution, or if insoluble, in suspension, is added cuprous chloride in the proportion of 2 to 3 per cent. of the total weight of ferrocyanide taken, and then an excess of dilute sulphuric acid—sufficient to yield a little free acid in the liquid over that required to form sodium or potassium bisulphate—and the mixture distilled. The whole of the ferrocyanide is decomposed and the cyanogen obtained as hydrocyanic acid, which may be absorbed in aqueous caustic alkali solution.

[1] H. E. Williams, *J.S.C.I.*, 1912 (31/5/12).

[2] J. Dewrance and Williams, E.P. 28,074 (24/12/08).

When the operation is complete, the residue in the still consists solely of a solution of ferrous sulphate and the sulphate or bisulphate of the base or bases of the ferrocyanide used, together with the excess free sulphuric acid. From this liquor the cuprous salt may be readily recovered by the addition of the requisite quantity of a soluble thiocyanate, the copper being instantly precipitated as the cuprous thiocyanate.

It is best, in carrying out the process, to dissolve the cuprous chloride in the smallest possible quantity of hydrochloric acid or a saturated solution of sodium or potassium chloride before adding to the still. By this means the cuprous chloride is added to the still in a more finely divided state, and the action is also greatly accelerated by the increased quantity of chloride in solution.

By this method cyanides may be obtained direct from cyanogen mud, or the residues from spent oxide after extraction of sulphur, without the intermediate formation of a soluble ferrocyanide.

Cyanides from Thiocyanates. Several methods have been worked out for the production of cyanides by using a thiocyanate as the raw material, in which the thiocyanate is directly converted into a cyanide without the intermediate formation of a ferrocyanide, and a few of these methods have been applied on a manufacturing scale.

These processes, which consist essentially in the removal of the sulphur of the thiocyanate, can be classed under two heads :

1. Those involving reduction.
2. Those involving oxidation.

D. S. Playfair in his investigations on the reduction of thiocyanates by metals found that this reduction could be readily accomplished in the fused state by both lead and zinc.[1] The latter metal yielded much better results, due to the fact that at the temperature of the reaction the lead was in the molten state, and therefore offered but small surface for reaction.

[1] E.P. 7764 (1890).

The carefully dried thiocyanate was fused at a temperature of about 400° C., and the metal added in as finely divided a state as possible, every effort being made to keep the reacting mass out of air contact. When the reaction was complete, the fused mass was cooled and lixiviated with water, filtered from the insoluble sulphide, and the aqueous solution evaporated to recover the cyanide.

When zinc was the metal used for the reduction, the cyanide solution was liable to be contaminated with the double zinc cyanide. The zinc could, however, be removed by the addition of the requisite quantity of pure sodium sulphide. Some considerable amount of cyanide has been made in this country by this process.

Attempts to reduce the thiocyanate by hydrogen have also been made by Playfair.[1] The reduction occurs, however, in two stages; in the first the thiocyanate is reduced, forming a cyanide with evolution of hydrogen sulphide, and in the second hydrocyanic acid is evolved and a sulphide left. These two reactions take place simultaneously once the action has started, the latter reaction beginning directly after the first had to a certain extent taken place, some of the hydrogen sulphide formed by the first reaction attacking some of the freshly formed cyanide and evolving hydrocyanic acid:

$$KCNS + H_2 = KCN + H_2S.$$
$$2KCN + H_2S = K_2S + 2HCN.$$

Thus with the thiocyanates of the alkali metals a mixture of hydrogen sulphide and hydrocyanic acid was evolved, and a fused mass of a cyanide and sulphide left. By substituting barium thiocyanate, however, most of the cyanogen was obtained as hydrocyanic acid.

These reactions were further investigated, and in the process of E. C. Rossiter, G. S. Albright and H. W. Crowther,[2] dry cuprous thiocyanate was well

[1] *J.S.C.I.*, 11, 14 (1893). [2] E.P. 4403 (1/3/01).

mixed with finely divided metallic copper, and heated gradually to 400° to 500° C. in a current of hydrogen, free from oxygen, carbon dioxide or moisture. The cyanogen was evolved as hydrocyanic acid, leaving a residue of cuprous sulphide; the latter body could be roasted to oxide, and a part dissolved in acid to prepare more cuprous thiocyanate, and part reduced to metallic copper.

In a subsequent patent [1] the process was made applicable to any thiocyanate, finely divided metallic copper being mixed with the dry thiocyanate, and the mixture heated gently, first to 150° C. and then gradually to 350° and finally 500° C.

That thiocyanates may be oxidized with formation of hydrocyanic acid and sulphuric acid was first observed by Hadow,[2] who found that such oxidizing agents as potassium permanganate, lead peroxide, manganese dioxide, or nitric acid would remove and oxidize the sulphur of a thiocyanate in aqueous solutions. Most of these oxidizing agents led to the production of a certain complex yellow compound called persulphocyanogen, with consequent loss of cyanogen; the yellow compound, however, found a limited market as a yellow dye under the name of Canarine.

Oxidation of the thiocyanate by electrolysis did not lead to any better results, the complex yellow compound being also formed.

A modification of these methods formed the basis of the patents of Rachen, Davidson and Brock,[3] who found that a yield of 98 per cent. of the total cyanogen as hydrocyanic acid could be obtained if excess of oxidizing agent was always present. The process was carried out by adding the thiocyanate in solution to an excess of heated but dilute nitric acid; thus avoiding the loss of cyanogen by formation of the complex yellow body canarine, which is generally

[1] E.P. 6226 (25/3/01). [2] *A.* (1858), **108**, 380.

[3] E.P. 10,476, 10,956 and 21,678 (1895); 19,767 (1898), and 12,180 (1900).

formed when the oxidizing agent is added to an excess of the thiocyanate.

The decomposition was carried out in earthenware vessels into which the dilute nitric acid was put and heated by steam. The thiocyanate solution was then run in slowly, the oxidation proceeding quietly, and quantitatively thus :

$$MCNS + 2HNO_3 = HCN + MHSO_4 + 2NO.$$

In the liquid leaving the decomposing vessel, the thiocyanate had been completely oxidized, but some hydrocyanic acid still remained in solution, which was subsequently driven off by heating in a second earthenware vessel.

The gases leaving the decomposer contained besides hydrocyanic acid and nitric oxide, some nitrogen trioxide together with a large amount of aqueous vapour. These gases were made to pass up a tower packed with flints or other suitable material down which a small trickle of water was flowing; all the nitrogen trioxide was absorbed in this stream of liquor, which was finally run into the decomposing vessel. The gases issuing from the scrubbing tower had lost but little of their heat, and were passed into a surface condenser, kept at a temperature of 50° to 60° C., when most of the steam was condensed together with a considerable proportion of the hydrocyanic acid (about 20 per cent. of the total). This dilute solution of hydrocyanic acid was returned to the second boiling vessel and the hydrocyanic acid again driven off. Thus the gases passing the condenser were rich in hydrocyanic acid and low in aqueous vapour, and were finally absorbed in an aqueous solution of caustic soda, which when saturated with the hydrocyanic acid was evaporated to recover the sodium cyanide.

The nitric oxide gas which was of course not absorbed by the caustic soda solution was mixed with an excess of air and passed upwards through scrubbers packed with flints, and down which a thin stream of water

was allowed to flow, and the so recovered nitric acid conducted into the decomposing vessel to oxidize more thiocyanate.[1]

The difficulties of this process were to prevent supersaturation of the caustic liquor with hydrocyanic acid, which would result in the formation of brown decomposition products, and consequent discolorisation of the cyanide ; and at the same time to leave no great excess of caustic alkali in the finished cyanide solution, so that a high strength alkaline cyanide could be obtained on evaporation. Also to prevent oxidation of the nitric oxide by air leakages before the gases passed through the caustic soda solution, for as the generated gases were excessively poisonous, it was necessary to maintain a slight vacuum in the apparatus, and thus any leaky connection would result in an inleak of air difficult to detect.

The thiocyanates required for the raw material were manufactured by a modification of the Gelis process by the reaction of carbon disulphide and ammonia under pressure. Thus the nitrogen of the cyanide was obtained from expensive ammonia, as in the synthetic methods of cyanide production of Bielby and Kessner, but although the latter process employed also the somewhat expensive metallic sodium, yet the cyanide was manufactured in the molten state, which more than counterbalanced the cost and loss of recovering the cyanides from aqueous solutions and the expense of first preparing the thiocyanates.

Some efforts were made to obtain a cheaper source of thiocyanates, but practically the only sources available were those resulting from the scrubbing of crude coal-gas with polysulphide liquors, and the mother liquor obtained in the manufacture of ferrocyanides from spent oxide of iron and cyanogen mud. But the total supply of this material is very limited and the product very crude.

Some modifications of the above process were suggested as more or less improvements. Thus according

[1] J. T. Conroy, *J.S.C.I.*, **18**, 432.

to Beringer,[1] some of the hydrocyanic acid is acted upon by the excess of nitric acid, and to remedy this he proposed to substitute barium nitrate instead of nitric acid, together with half the theoretical sulphuric acid necessary to decompose the nitrate, the remaining sulphuric acid being developed by the oxidation of the sulphur of the thiocyanates, thus with barium thiocyanate :

$$Ba(CNS)_2 + 2Ba(NO_3)_2 + H_2SO_4 = 2HCN + 3BaSO_4 + 4NO.$$

The barium nitrate was to be dissolved in water and heated in a decomposing vessel, and a solution of barium thiocyanate with the calculated quantity of sulphuric acid gradually added.

Accepting the statement that some of the hydrocyanic acid was lost by oxidation with excess of nitric acid in Rachen's process, it is doubtful whether the quantity so lost was appreciable if the conditions of the process were carefully regulated.

A modification of Rachen's process was patented by J. Tcherniac,[2] in which the nitric oxide resulting from the oxidation of the thiocyanate by nitric acid was oxidized by air before the removal of the hydrocyanic acid.

Air or oxygen was to be blown through the solution containing the dilute nitric acid to which the thiocyanate solution was slowly added. The evolved gases were first scrubbed in a tower and passed over anhydrous sodium sulphate or alumina, etc., to remove nitric acid, and finally over heated sodium or potassium carbonate or their hydroxides, but preferably the latter. When caustic soda was used it was to be heated to a temperature of 200° C. at first and then gradually raised to 300° C.

[1] E.P. 18,565 (14/9/99).
[2] E.P. 17,976 (18/2/02), and 17,449 (11/8/03).

CHAPTER XII

MANUFACTURE OF CYANIDES FROM NITROGEN OR AMMONIA

THE problem of the production of cyanides by using the atmospheric air as a source of nitrogen has occupied the attention of numerous investigators since the discovery in 1837 by Prof. Clark of the formation of potassium cyanide in blast furnaces, an observation which was confirmed some years later by Redlenbacker. This subject was then investigated by Bunsen and Playfair, who found that the cyanide was formed in the hottest part of the furnace just above the tuyères,[1] and that it was produced only at the temperature necessary for the liberation of metallic potassium.

From that time to the present day a great number of processes have been patented to produce cyanides using the nitrogen of the air, several of which have been worked on a commercial scale, but unfortunately without financial success. The reason of these failures has not been that the cyanide could not be produced, but the enormous fuel consumption to maintain the excessive high temperature necessary, and the consequent rapid destruction of plant from this cause. The amount of potassium cyanide obtained was comparatively small and quite out of all proportion to the very large amount of material and fuel used. Again, in practically all these processes, the product was obtained intermixed with a large proportion of other materials, from which it was necessary to separate the cyanide by lixiviation, and conversion into ferro-

[1] *Brit. Assoc. Report* (1845), 185.

cyanide, or to recover it from the aqueous solution, thus adding enormously to the cost of the cyanide.

Just before the publication of Bunsen and Playfair's investigations above mentioned, a process was worked in France by Possoz and Boissièrre,[1] but after a year's working it was transferred to Newcastle for the purpose of obtaining cheap fuel, where it was worked by Bramwell and Co., prussian blue manufacturers, and a great number of improvements introduced. In the process as modified by Bramwell, wood charcoal was soaked with a strong solution of potassium carbonate and dried, and then placed in a series of vertical earthenware retorts and raised to a very high temperature, while air was passed through the retorts. When the reaction was complete the contents of the retorts were emptied out, lixiviated with water and the crude cyanide solution converted into ferrocyanide, the latter being recovered by crystallization. This process was worked for two years and about 300 tons of prussiate of potash per year were made. At the end of that time the plant was closed down, the working cost and the wear and tear on the plant being found excessive.

The substitution of barium oxide and carbon in the place of the mixture of potassium carbonate and carbon, in the process of Margueritte and de Sourdeval,[2] proved to be a good means of absorbing nitrogen from the atmospheric air, and in some respects superior to the employment of potassium carbonate, probably chiefly on account of the less fusible character of the barium oxide.

Some thirty-five years later Readman[3] again attacked this problem, and in order to economize fuel and to prevent the rapid destruction of the apparatus —which had always taken place when the retorts were externally heated to the very high temperature necessary, and had rendered these processes so unsuccessful—he charged the retorts with carbon, intimately

[1] E.P. 9985 (1843).
[2] E.P. 1171 (1860).
[3] E.P. 6621 (1894).

mixed with an alkali, and heated the mixture in a current of nitrogen by means of electricity, using a carbon electrode. Thus by internally heating comparatively little injury to the retorts and apparatus took place.

This process was worked at Leven, Fifeshire, by the Scottish Cyanide Company, who erected extensive, up-to-date and well-equipped works. Barium carbonate was first mixed with fine coal and coked, and this granular product fed into a vertical retort and the mixture heated to a high temperature by means of an alternating current passing between carbon electrodes, one of which was suspended in the retort in the form of a carbon rod, and the other consisting of carbon blocks fitted near the bottom of the retort. During the heating, producer gas was passed upwards through the mass. The process was a continuous one, the coked mixture being fed in at the top, and the cyanized mixture removed from the bottom by mechanical appliances. A temperature of at least 1400° C. was found necessary to obtain a large absorption of nitrogen.

The cooled cyanized product was then lixiviated with water to remove all soluble salts, the soluble barium salts precipitated by sodium carbonate and bicarbonate, and filtered from the insoluble barium carbonate, which was washed and dried, mixed with ground coal, carbonized and reintroduced into the electric furnace. The clear filtrate was then evaporated in vacuo, and crystals of hydrated sodium cyanide obtained. These crystals were dried and dehydrated by heating under reduced pressure, and the anhydrous powder briquetted by hydraulic pressure.

As barium cyanide when heated to a high temperature is partially converted into barium cyanamide and free carbon according to the reversible equation :

$$Ba(CN)_2 \rightleftharpoons BaCN_2 + C$$

some of the nitrogen absorbed must have been lost in this form.

This process, which was worked from 1899 to 1907, proved to be a financial failure, for although a marked advance over the previous efforts in the utilization of the nitrogen of the air for the formation of cyanide, yet it was unable profitably to make cyanides at the lower prices then ruling.

While the process above described was being developed, the problem was attacked in another direction by Frank and Caro,[1] who discovered that the carbides of the alkaline earths absorbed nitrogen when heated to a suitably high temperature in an atmosphere of that gas.

When barium carbide was used the resulting product consisted of a mixture of barium cyanide and cyanamide. If this mixture was fused with sodium carbonate and carbon the whole of the nitrogen was obtained in the form of cyanide which may be dissolved in water and converted into ferrocyanide, from which pure sodium cyanide could be obtained by fusing the dehydrated sodium ferrocyanide with metallic sodium. Six-sevenths of the total nitrogen absorbed could be recovered in this way as cyanide, but this method proved much too expensive.[2]

On repeating these experiments with calcium carbide, a product which was at that time being manufactured on a large scale, the results were at first disappointing, for no cyanide was obtained, the product consisting essentially of calcium cyanamide and free graphitic carbon, entirely free from cyanide, thus :

$$CaC_2 + N_2 = CaCN_2 + C.$$

It was afterwards shown that calcium cyanamide was of great value as an artificial manure in place of sodium nitrate, and that it would also serve as a raw material for the preparation of other valuable nitrogen compounds. For these reasons the manufacture of

[1] E.P. 15,066 (1895).

[2] G. Erlwein (1903), 5th Int. Kongress angew Chem., Berlin, i. 646.

this product was conducted on a large scale at many of the industrial centres of the world, particularly where water-power was available.

Many experiments were made to treat the cyanamide in such a manner as to cause the carbon to recombine with the cyanamide and so form calcium cyanide or other cyanides. These experiments were to a certain extent successful, and a patent was taken out by Dr. G. Erlwein and Prof. A. Frank in 1902.[1] According to this patent the cyanamide was to be fused with a metallic chloride, preferably sodium chloride, in a suitable manner in specially constructed furnaces.

In the author's experience, the fusion of the cyanamide with sodium chloride in an ordinary manner resulted only in a partial conversion of the cyanamide into cyanide, the amount of the latter varying according to the proportion of sodium chloride employed. Increased proportions of the salt resulted in the formation of increased quantities of the cyanide, and that the conversion only approached completion when the amount of sodium chloride became proportionately large.

It is probable that the cyanide existed in the melt as sodium cyanide, the sodium chloride reacting with the calcium cyanamide to produce first sodium cyanamide and calcium chloride thus :

$$2NaCl + CaCN_2 = CaCl_2 + Na_2CN_2.$$

The sodium cyanamide then immediately combines with the carbon to form sodium cyanide according to the well-known reaction :

$$Na_2CN_2 + C = 2NaCN.$$

The two reactions may be expressed together :

$$2NaCl + CaCN_2 + C \rightleftharpoons CaCl_2 + 2NaCN.$$

Now calcium cyanide does not appear to exist in the solid state at high temperatures, but immediately splits up into calcium cyanamide and carbon. The sodium cyanide when once formed would react with

[1] 708,333, U.S.A. Pt.

the calcium chloride to form sodium chloride and calcium cyanamide and free carbon, so that the reaction expressed by the above equation is a reversible one, and the amount of nitrogen combined as cyanamide and cyanide will vary with the ratio of sodium chloride to calcium cyanamide.

By selecting an appropriate furnace with special appliances for melting and cooling the material, Dr. N. Caro [1] claimed that the difficulties of the process were overcome, and the conversion of the cyanamide into the cyanide took place quantitatively. It was, however, necessary that the cyanamide should be free from calcium carbide.

By using sodium carbonate, however, the reaction would not be a reversible one and would be expressed by the equation :

$$Na_2CO_3 + CaCN_2 + C = 2NaCN + CaCO_3.$$

Strontium carbide* also absorbs nitrogen when heated to 1000° to 1200° C. in an atmosphere of that gas and as is the case with barium, a mixture of cyanide and cyanamide is produced.[2]

Using lithium carbide a mixture of cyanide, cyanamide and dicyandiamide is produced, the maximum absorption of nitrogen takes place at 925° C.[3]

The above described processes for the production of cyanide by means of the nitrogen of the air, are those which were tried on a commercial scale. A large number of other proposals were also made, but so far as is known they were never worked on large scale operations, and the best known of these processes are described below.

J. Pfluger [4] heated carbon and an alkali in thin layers with just enough space above to admit only as

[1] 7th Int. Cong. App. Chem., 1909, Sect. ii. 111B, IVA—vii. xx.

[2] S. A. Tucker and Y. T. Yang, 8th Int. Cong. App. Chem., 1912, **21**, 121–26.

[3] S. A. Tucker and H. R. Moody, *J. Am. Chem. Soc.* (1911), **33**, 1478–85.

[4] E.P. 18519 (29/10/94).

much air as was required for local combustion. This process was said to differ from those previously described in that the operation was completed in a shorter time by using air, and not more or less oxygen free air.

In the process of J. D. Darling [1] a combination is made of the methods of utilizing the nitrogen of the air, and the manufacture of cyanides from ammonia and metallic sodium. An alkali hydroxide or carbonate is heated to a high temperature with carbon in the presence of nitrogen, and the resulting " cyanized " carbon then heated in conjunction with metallic sodium, and converted into cyanide by passing dry ammonia gas through the molten mass; or both nitrogen and ammonia are passed through the molten metal containing a mixture of alkali and carbon ; [2] or the ammonia is passed through molten metallic sodium and the resulting amide heated with the cyanized carbon.[3]

Cyanides are said to be produced when nitrogen, or a mixture of nitrogen with hydrogen or carbon monoxide or both, is passed into molten iron kept saturated with carbon and covered with a layer of coke.[4]

The barium cyanamide formed in the process of Margueritte and de Sourdeval or when nitrogen is passed over heated barium carbide, is said to be converted into barium cyanide by treatment with a current of a gas containing carbon compounds other than carbon dioxide, at a temperature below 1200° C.[5]

Sir J. W. Swan and J. A. Kendall [6] proposed to introduce nitrogen and the alkaline carbonate or hydroxide in a regular manner into a reaction chamber containing carbon heated to a very high temperature. Alkaline cyanide in the form of vapour is obtained

[1] U.S.A. Pt. 698462 (29.4.02), and E.P. 9350 (1900).
[2] U.S.A. Pt. 698463.
[3] U.S.A. Pt. 698464.
[4] G. Erlwein, G.P. 199973 (6.6.06).
[5] Badesch Amlin and Soda Fabrik, E.P. 22039 (5/10/06).
[6] E.P. 26258 (12/11/09).

which is passed into a condensing chamber from which it flows in the molten state, the high temperature necessary being obtained by means of oil fuel.

When a mixture of nitrogen, hydrogen and hydrocarbon vapour is heated to a high temperature, hydrocyanic acid is formed which may be extracted from the cooled gases, and the gaseous residue returned to the reaction chamber. The excess of hydrogen formed by the decomposition of the hydrocarbons is eliminated by diffusion or oxidation.[1]

CYANIDES FROM SCHLEMPE (BEET MOLASSES)

In the manufacture of sugar from beetroots a residual mother liquor is obtained, containing all the organic and inorganic impurities of the original juices together with some sugar. These molasses are usually used as a cattle food. In Germany, however, a large proportion of the beet sugar molasses is treated with strontia, which removes the bulk of the sugar, as a strontium sucrate, and the residue is concentrated as far as possible to a thick syrup.

This residue or Schlempe as it is called, contains a large proportion of organic and inorganic compounds, the latter of which consist principally of potassium salts, while about 4 per cent. of nitrogen is contained in the organic constituents principally in the form of betaine, $OH.N(CH_3)_3.CH_2.COOH$.

The earliest attempt to utilize this residue was made by Vincent about the year 1880. He subjected it to dry distillation in an iron retort and obtained a distillate consisting of ammonia, methyl alcohol, one or more of the methylamines, and a carbonaceous residue containing considerable quantities of potassium carbonate.

That methylamine was decomposed at a red heat into ammonia, hydrocyanic acid and hydrogen was

[1] Soc. Anon. pour l'Industrie de l'Aluminium, F.P. 417794 (2/7/10).

first shown by Wurtz, while Wilm Orlieb and Müller found that trimethylamine was also decomposed in a similar manner, forming ammonia, hydrocyanic acid and a hydrocarbon. This process was actually worked for a few years, the methylamine obtained in the distillation of "Schlempe" was passed through red-hot tubes, and the resulting vapours containing ammonia and hydrocyanic acid, passed first into dilute sulphuric acid to remove the ammonia, and then into a solution of potassium and ferrous hydroxide, in order to obtain ammonium sulphate, and potassium ferrocyanide respectively.[1]

Some fourteen years later Dr. Bueb[2] patented a process for this conversion, in which the vapour obtained in the distillation of the schlempe is conducted directly into brick flues which are raised to a red heat, and the exit vapours passed into a solution of ferrous sulphate in order to arrest both the ammonia and hydrocyanic acid. These flues, however, rapidly became blocked owing to the formation of a heavy deposit of carbon.

In the subsequent improvements this difficulty was overcome by passing the vapours from the schlempe through firebrick checker-work which had been previously heated by direct firing; one furnace being heated while another was being used for the conversion of the methylamines, and thus the trouble caused by the carbon deposit avoided, for the carbon left by one operation was burnt off in the subsequent reheating. The vapour, after removal of the tar, was scrubbed free from ammonia by sulphuric acid, the hydrocyanic acid absorbed in a scrubber of sodium hydroxide, and the sodium cyanide recovered by evaporating the solution under vacuum, and drying the hydrated crystals also under reduced pressure. The anhydrous powder is pressed into briquettes of sodium cyanide equivalent to 120 to 125 per cent. potassium cyanide; or the hydrocyanic acid vapour was passed into an

[1] E.P. 2844 (1879).

[2] Reichardt and Bueb, E.P. 7171 (3/4/95); 26259 (1898).

alcoholic solution of sodium hydroxide, the sodium cyanide which is practically insoluble in alcohol, obtained as a white crystalline powder containing little if any combined water, and therefore more easily dried.

The best temperature for the decomposition of the methylamine is, according to the researches of Voerkelium between 800° and 1000° C. when an almost quantitative yield of hydrocyanic acid is obtained from mono-, di- and trimethylamine when the gases are passed through a heated porcelain tube at a great rate. At a slower rate some nitrogen is formed by decomposition of the hydrocyanic acid :

$$NH_2CH_3 = HCN + 2H_2.$$
$$NH(CH_3)_2 = HCN + H_2 + CH_4.$$
$$N(CH_3)_3 = HCN + 2CH_4.$$

The formation of hydrogen leads to a secondary reaction with destruction of the formed hydrocyanic acid and formation of ammonia :

$$HCN + 3H_2 = NH_3 + CH_4.$$

Trimethylamine may be directly decomposed with formation of sodium cyanide by passing the dry gas through molten metallic sodium, a hydrocarbon, carbon and hydrogen being formed at the same time.[1] The sodium cyanide may be separated from the carbon by filtration ; or the formation of the carbon may be avoided by the addition of disodium cyanamide, or by allowing ammonia to pass into the fused metallic sodium along with the trimethylamine.

CYANIDES FROM CARBON AND AMMONIA

In the synthetic process for the manufacture of cyanides worked out by Dr. Siepermann, ammonia was substituted for the nitrogen gas of the earlier investigators.[2]

[1] Deutsch Gold und Silber Scheide—Amstalt ; E.P. 9375 (18/8/10).

[2] D.R.P. 38012 (10/3/86) ; E.P. 13697 (1889) ; 13732 (1893). and 9350 and 9351 cf. (1900).

Charcoal and potassium carbonate are mixed with sufficient of the former to prevent the mass fusing on ignition. Two parts by weight of charcoal to one part of the alkali is the proportion usually used, and the mixture placed in the upper part of a vertical retort, and heated to a dull red heat while dry ammonia gas is passed through, which reacts with the potash and carbon to form potassium cyanate. When this reaction is complete, the mixture is allowed to pass into the lower part of the retort, and heated to a much higher temperature, whereby the carbon reduces the cyanate to cyanide with evolution of carbon monoxide or dioxide.

The reactions which take place are in the main explained by the two equations given below :

(1) $K_2CO_3 + NH_3 = KCNO + KOH + H_2O$.
(2) $KCNO + C = KCN + CO$.

Careful research has shown however that these reactions are not quite so simple as those shown by the above equations, and that intermediate products are first formed. For example the first action of the higher temperature is to cause the carbon to react on the cyanate to form dipotassium cyanamide :

$$2KCNO + C = K_2CN_2 + 2CO,$$

and that this cyanamide then reacts with carbon to form cyanide :

$$K_2CN_2 + C = 2KCN.$$

The product obtained after the completion of the above reactions is raked out of the retort and cooled out of air contact. This material contains besides the cyanide, the excess of carbon, and the carbonate and cyanate of potassium. In order to obtain the cyanide it must be systematically lixiviated, and the potassium cyanide precipitated by dissolving potassium carbonate in the strong solution, the former being less soluble in strong solutions of potassium carbonate than in pure water ; or the liquor evaporated nearly to dryness and the bulk of the potassium carbonate removed

by treatment with a little hot water. The remainder is then washed with ice cold water which dissolves the potassium cyanate and any remaining carbonate, leaving a residue of almost pure potassium cyanide.

The product of this process was a deliquescent mass and was fused with the cyanide obtained by fusing anhydrous ferrocyanide with metallic sodium. It was first put on the market in 1892.

While Siepermann's process was being worked out, Dr. Bielby also devised a process for the synthetical production of cyanides [1] from ammonia, carbon and carbonate of potash. This process, however, differed materially from that of Siepermann, although the same materials were employed.

The process consisted in passing dry and pure ammonia gas through a molten mixture of 55 to 60 parts of pure dry potassium carbonate, 20 to 25 parts of carbon and 20 parts of potassium cyanide, the amount of carbon being just sufficient to leave a slight excess over that required to form potassium cyanide. It is on this point that the process differs so essentially from, and is such a marked improvement over, the process of Siepermann. For whereas in the latter process sufficient carbon is added to prevent fusion, and so render necessary the extraction of the melt with water, and the recovery of the cyanide from the aqueous solution with all its difficulties; in the former process the carbon is reduced to a minimum and the cyanide obtained in the molten state readily purified by a simple filtration from the excess carbon.

The potassium cyanide is added in the first operation to assist fusion and to reduce the temperature of the melting-point of the mixture. This reduction of the melting-point of the mixture is a very important point, for it has been shown [2] that ammonia rapidly decomposes into its elements at temperatures above 500° C.

[1] E.P. 4820 (18/3/91).

[2] Ramsay and Young, *T.C.S.* (1884), 88; Bielby and Henderson, *T.C.S.* (1901), 1245; Readman, *J.S.C.I.* (1889), **8**, 757, and Conroy, *J.S.C.I.* (1896), **15**, 12.

In practice the carbon is not all added at once, but gradually, as required during the progress of the operation, so that the material may be kept always in as fluid a state as possible. The ammonia is forced through the liquid under pressure.

When the operation is considered complete, the melt is filtered while still in the molten state from the small amount of carbon, and then run into moulds. This process produced a pure white cyanide of high strength, having the same crystalline appearance and structure as that obtained by smelting potassium ferrocyanide with metallic sodium.

Sodium cyanide can, of course, be produced, and is so produced with equal ease by substituting sodium carbonate for the potassium salt.

It has been estimated that the output by this process in the year 1899 was about half the total production of Europe.[1]

In the year 1894, H. Y. Castner obtained two patents [2] for the manufacture of cyanides by the direct combination of carbon, nitrogen or ammonia, and an alkali metal, the latter being prepared separately. The action was said to take place at a much lower temperature, and larger yields obtained than when the alkaline hydroxides or carbonates were used. Nitrogen gas was passed up from below through a retort filled with charcoal and heated in a furnace, and the alkali metal added in at the top.

This process was considerably modified in a subsequent patent [3] in which the process is carried out in two stages. First, pure dry ammonia gas is passed over metallic sodium heated to between 300° to 400° C. forming hydrogen and a sodium amide :

$$2NH_3 + 2Na = 2NaNH_2 + H_2.$$

The amide so formed is then fused in contact with

[1] Dr. G. T. Bielby, 5th Int. Cong. App. Chem., Berlin.
[2] E.P. 12218 and 12219 (23/6/94).
[3] Castner, 21732 (10/11/94).

carbon to form cyanide with a further evolution of hydrogen :

$$NaNH_2 + C = NaCN + H_2.$$

The reactions which actually take place are not quite so simple as those expressed above ; the sodium amide when first brought into contact with the carbon at a temperature of 550° to 600° C., forms disodium cyanamide :

$$2NaNH_2 + C = Na_2CN_2 + 2H_2,$$

which reacts with more carbon as the temperature rises to 750° to 800° C. to form sodium cyanide :

$$Na_2CN_2 + C = 2NaCN.$$

At the time of the publication of this process metallic sodium was a much too costly raw material for this process to have been a commercial success, but some few years later the price of metallic sodium dropped considerably owing to improved methods of production, and this process which had been neglected for a few years was revived and worked with commercial success.

The conversion of ammonia into cyanide may be accomplished in many other ways, as the following list of patent methods show, although there is no evidence that any of them passed the experimental stage.

P. R. de Lambilly [1] proposed to pass carbon monoxide saturated with ammonia gas through a series of tubes filled with a porous substance such as pumice, and heated to 100° to 120° C. in order to obtain formamide :

$$NH_3 + CO = H.CO.NH_2.$$

This product was then to be passed through a second series of tubes heated to at least 210° C. to obtain hydrocyanic acid :

$$H.CONH_2 = HCN + H_2O.$$

By mixing sodium carbonate or bicarbonate with a

[1] E.P. (20/2/93), 3735 ; F.P. 232697 (1893).

reducing agent such as zinc or manganese, and heating the mixture in a current of ammonia, sodium cyanide is formed which may be washed out from the zinc oxide : [1]

$$NH_3 + Na_2CO_3 + Zn = NaCN + ZnO + NaOH + H_2O.$$

If carbon dioxide is mixed with the ammonia the sodium hydroxide is converted into carbonate and the reaction is then said to go to completion.

A. and J. Gordon [2] carefully mixed potassium sulphate with carbonaceous matter preferably of animal origin, and heated the mixture to a very high temperature in a furnace while ammonia was passed in with the air blast. Potassium cyanide is formed and volatilizes, and is recovered by condensing the vapour.

J. R. Moise [3] ignited a mixture of anhydrous borax and ammonium chloride in order to obtain boron nitride which was washed free from sodium chloride by hot water, and then fused with a mixture of potassium carbonate and carbon to obtain potassium cyanide :

$$4BN + 3K_2CO_3 + 2C = K_2B_4O_7 + 4KCN + CO_2.$$

The cyanide was to be recovered by solution in alcohol or converted into ferrocyanide by the usual means.

Ammonium cyanide may be produced by heating two volumes of ammonia and one volume of carbon monoxide : [4]

$$2NH_3 + CO = NH_4CN + H_2O.$$

Carbon dioxide or producer gas may be used instead of the carbon monoxide.

H. C. Woltereck.[5] A gaseous mixture of ammonia and a hydrocarbon is to be passed over a suitable catalytic agent such as heated platinized pumice

[1] J. Hood and A. Salaman, E.P. 21239 (8/11/93).
[2] E.P. 16750 (6/9/93)
[3] E.P. 19201 (12/10/95).
[4] E.P. 5037 (7/3/99).
[5] E.P. 19804 (10/9/02).

when hydrocyanic acid is formed. The platinized pumice may be replaced with freshly reduced iron.

J. Grossmann [1] proposed to produce cyanides by passing dry ammonia gas over a mixture of an alkali and sulphur, or an alkaline sulphide and carbon heated in a retort.

Dr. G. Beindl [2] prepared hydrocyanic acid catalytically by passing ammonia and a hydrocarbon vapour over a coil of wire netting made of a number of metals.

C. E. Acker [3] passed dry ammonia gas into a molten sodium lead alloy obtained by electrolysing sodium chloride upon a lead cathode, and in the presence of charcoal. According to U.S.A. Pt. 914214, 2/3/09, sodium amide is made by passing ammonia into molten sodium lead alloy, or calcium nitride by passing nitrogen into calcium lead alloy, which may be converted into cyanide or cyanamide by heating with carbon.

A number of patents have been granted from time to time for the manufacture of cyanides in which other sources of nitrogen are used in place of atmospheric air or ammonia, amongst the most interesting of which are the following.

W. Kerp [4] fused a mixture of sodium acetate and sodium nitrate to obtain sodium cyanide, an equal weight of soda ash being added to reduce the violence of the action.

G. Kraemer [5] heated anthracene residues containing carbazol to 280° to 340° C. with sodium or potassium hydroxide in a suitable manner, and the crude potassium carbazol which separates is converted into sodium or potassium cyanide by heating to bright redness in a suitable vessel with the addition of alkali.

Vidal [6] strongly heated phospham with sodium or

[1] E.P. 24011 (2/12/99).
[2] E.P. 18949 (17/8/09).
[3] U.S.A. Pt. 914,100 (2/3/09).
[4] *Ber.* **30**, 610–12.
[5] E.P. 16529 (30/8/94).
[6] E.P. 9215 (10/4/94).

potassium carbonate whereby a phosphate and a cyanate are produced :

$$PN_2H + 2K_2CO_3 = K_2HPO_4 + 2KCNO.$$

The addition of carbon to the melt produced a cyanide, and of sulphur a thiocyanate.

If the phospham is heated with potassium oxalate cyanogen is liberated :

$$P.N_2H + K_2C_2O_4 = K_2HPO_4 + (CN)_2,$$

but if heated with the acid oxalate with the addition of carbon, hydrocyanic is liberated :

$$P.N_2H + KHC_2O_4 + C = KPO_3 + 2HCN + CO,$$

or if heated with formic acid instead of the oxalate :

$$PN_2H + 2H_2CO_2 = H_3PO_4 + 2HCN.$$

Huntington [1] produced hydrocyanic acid by igniting a mixture of nitric oxide and acetylene gas in a cylinder :

$$C_2H_2 + NO = HCN + CO + H.$$

Hoyermans [2] heated the two gases, nitrogen and acetylene, in an electric furnace to obtain hydrocyanic acid :

$$C_2H_2 + N_2 = 2HCN.$$

C. F. Cross and T. Young [3] obtained a cyanide together with an oxalate, by first preparing a mixture of a nitrate and an organic compound such as aldehyde or sugar, together with an alkali, or alkaline earth, and a little water, and heating the mixture gradually to 150° to 170° C.

W. E. Cooper [4] treated humas in the form of peat or farmyard manure with nitric acid and distilled the mixture. Hydrocyanic acid was said to be obtained in the distillate together with other nitrogenous compounds, and a residue left which might be utilized as a manure.

[1] E.P. 14855 (6/8/95).
[2] E.P. 28077 (19/12/02).
[3] F.P. 294979 (5/12/99).
[4] E.P. 2047 (26/1/06).

G. Müller [1] proposed to produce cyanides by igniting a nitrate or a nitrite with excess of charcoal.

The Badische Anilin and Soda Fabrik [2] prepared titanium nitride and carbonitride, which was then to be heated with carbon and an alkali or alkaline earth hydroxide. With alkalis only cyanides are produced, but with barium a mixture of cyanide and cyanamide and with calcium only cyanamide is obtained.

THE RECOVERY OF ALKALINE CYANIDES FROM AQUEOUS SOLUTIONS

The recovery of the alkaline cyanide from aqueous solutions is attended with considerable difficulty. A difficulty which contributed largely to the commercial failure of many of the processes described above, particularly those in which atmospheric nitrogen was used.

The cyanide solution must be evaporated with great care under reduced pressure to prevent loss of hydrocyanic acid by volatilization due to dissociation of the cyanide or by conversion into ammonia and formic acid by hydrolysis. These two reactions may be expressed thus :

$$NaCN + H_2O = HCN + NaOH.$$
$$NaCN + 2H_2O = NH_3 + NaHCO_2.$$

Some considerable quantity of hydrocyanic acid may be driven off with the steam if the cyanide solution is evaporated under atmospheric pressure, but little, however, is lost in this way if the evaporation is accomplished under greatly reduced pressure.

The second reaction, hydrolysis of the cyanide to ammonia and a formate, takes place to a very limited extent, in spite of the statements frequently made in text-books to the contrary, and with care the loss from this reaction is very small. If, however, cyanide

[1] G.P. 196372 (7/2/07).

[2] G.P. 200986 (31/3/07), and E.P. 1841 (27/1/08).

solutions are kept for some time, some appreciable loss may take place from this cause.

If the cyanide solution is contaminated by salts other than small quantities of the hydroxide or carbonate of the alkali, the recovery of the cyanide by crystallization is very difficult, and in most cases practically impossible, and it must, therefore, be converted into a ferrocyanide which may be more readily separated by crystallization, or the cyanide decomposed by the addition of an acid, and the liberated hydrocyanic acid distilled off into a solution of a pure alkaline hydroxide. Sodium or potassium bisulphate, or a salt such as magnesium chloride may be used in place of the acid to liberate the hydrocyanic acid.

When the solution is obtained by saturating a pure solution of sodium hydroxide with hydrocyanic acid, sufficient of the latter is allowed to be absorbed until but little excess of alkali remains. The solution is then evaporated down gently under greatly reduced pressure in an efficient vacuum evaporator, and cooled, when crystals of sodium cyanide dihydrate separate. These crystals are then removed from the solution and freed from mother liquor as much as possible by a centrifugal machine, and carefully dried under reduced pressure, the resulting white loose anhydrous powder is compressed into briquettes by a pressure of about three tons per square inch.

Various processes have been patented to overcome the difficulties of this operation, and to expedite the recovery: thus J. D. Gilmour [1] proposed to pass warm air over the cyanide to be dried, and then on to a condenser where it deposited its moisture. This air was afterwards again warmed and repassed over the cyanide, and by using the same air over and over again decomposition by carbon dioxide is largely prevented. For a similar purpose it was proposed by the Chemische Fabrik Schlempe Gas [2] to surround each particle of the cyanide with a little free alkali,

[1] E.P. 29922 (29/12/96). [2] E.P. 29383 (24/12/06).

the cyanide was to be separated from the solution under such conditions that the alkali crystallized along with the cyanide, thus protecting the cyanide from the action of the air.

Efforts were also made to reduce the cost of the evaporation of the aqueous solution. In the patent of T. Tcherniac [1] this was to be accomplished by breaking up solid caustic soda into small pieces and heating it to a temperature of about 200° C. which is below its melting-point, but sufficiently high to expel moisture, in order to obtain anhydrous cyanide direct from hydrocyanic acid and caustic soda, without the medium of aqueous solution. Thus saving the cost and loss of recovering the product from aqueous solutions.

It is probable that some technical difficulty was met with in the application of this process, possibly due to decomposition of some of the hydrocyanic acid in the presence of water vapour at the temperature necessary, for some few years later this investigator proposed the following plan for dealing with aqueous cyanide solutions.[2] The hydrocyanic acid was to be absorbed in the alkaline solution containing sufficient caustic soda to form a 30 per cent. solution of sodium cyanide. In this solution was dissolved an equal quantity of caustic soda and the solution again just saturated with hydrocyanic acid—as free from water as possible. On again dissolving the same quantity of solid caustic soda in this cyanide solution, about one-half of the total cyanide in solution separated in a more or less dehydrated state which could be freed by centrifugal action from the bulk of the mother liquor, and dried by gently heating in a vacuum. The mother liquor was then again saturated with hydrocyanic acid, and more sodium cyanide caused to separate by dissolving a further quantity of solid caustic soda in the liquid. These operations were to be repeated, the solution being kept to approximately the same bulk by evaporating under reduced pressure when necessary.

[1] E.P. 17449 (11/8/03). [2] E.P. 11371 (15/5/06).

It has been stated that the hydrated crystals of sodium cyanide obtained on evaporating the aqueous solution may be converted into the anhydrous compound [1] if the evaporation is made to take place in the presence of potassium cyanide.

This, however, could also be accomplished without the aid of potassium cyanide by crystalling the sodium cyanide from the solution above 34° C., the melting-point of the hydrate.

According to the patent of the Chem. Fabrik Schlempe [2] the cyanide crystals are to be moulded under pressure first and then heated in a vacuum for some time.

To separate cyanides from crude mixtures containing other salts, such as the melt obtained in the fusion of calcium cyanamide with sodium chloride, or in the manufacture of cyanide by heating sodium or potassium carbonate and charcoal in an atmosphere of ammonia or nitrogen, the aqueous solution may be heated under reduced pressure with the necessary quantity of an ammonium salt such as ammonium carbonate [3] instead of the usual method of distillation with an acid.

The substitution of acetic acid for the mineral acid in the recovery of hydrocyanic acid from crude solutions was proposed by Ampère Electro Chemical Co, N.J., U.S.A.[4] and the crude acetate solution to be evaporated to dryness, after the hydrocyanic had all been distilled off, and the dry material ignited to produce acetone. The alkaline carbonate resulting being mixed with more carbon and used again in the furnace in conjunction with nitrogen to form more cyanide.

In the process of T. Wilton [5] the crude cyanide is to

[1] Strassfurter Chemische Fabrik vormal Vorster and Gruneburg, E.P. 23124 (15/11/01).

[2] E.P. 18096 (9/8/07).

[3] Badisch Anilin and Soda Fabrik, E.P. 22540 (19/10/04).

[4] U.S.A. Pt. 719223 (27/1/03).

[5] E.P. 7107 (4/4/99).

be purified by means of liquefied ammonia under pressure which may either dissolve the cyanide or the impurity according to the nature of the latter.

The commercial application of the simple cyanides covers a varied field, hydrocyanic acid, the cyanide and oxycyanide of mercury, the zinc mercuric cyanide (Lister's antiseptic), etc., are used in medicine. Hydrocyanic acid is used in agriculture as an insecticide, particularly in America; and the cyanides of potassium and sodium in photography (as a fixing agent), in electro-plating, and in the extraction of gold and silver from their ores.

The most important application is in the metallurgy of gold. Formerly potassium cyanide only was used for the extraction; it was succeeded by a "double" salt, a mixture of sodium and potassium cyanide, but at the present day, pure high strength sodium cyanide is practically the only cyanide used in the gold industry. It is possible that future development may be in the direction of the use of calcium cyanide in solution, manufactured on the spot, at each centre of consumption.

The cyanide process for the extraction of gold has been described in a number of very excellent works, but the following synopsis of the process may not be out of place.

It had long been known that a solution of an alkaline cyanide was a solvent for gold, but it remained for McArthur and Forrest to work out an industrial method based on this reaction.

The principle of the process is simple, and rests on the fact that finely divided gold is slowly dissolved by a dilute cyanide solution in contact with the air: and that the gold may be recovered by passing the double gold cyanide solution over a large surface of metallic zinc.

The cyanide process was first applied on a practical scale in New Zealand, but it was on the Witwatersrand field in the Transvaal that it received its great industrial development. The general method of carrying out

the process in the latter district is briefly described below.

The ore, when brought to the surface, is washed and shot upon a revolving table or belt conveyer, and the waste ore (quartzite) picked out by hand from the gold-bearing ore (banket) and thrown aside. The ore is then fed into an ore breaker, where it is reduced to a small size, conveyed by a belt conveyer to the stamp shed, fed under the stamps with a stream of water, and crushed to a very fine state of division.

The sludge of ground ore and water leaving the screens of the mill, is made to flow in a thin stream over amalgamation tables, which consist of thin sheets of copper about 12 ft. long by 4 ft. 6 in. wide, amalgamated with mercury on the upper surface, and fixed on a suitable sloping framework. During the passage of the sludge over these tables, the heavier and coarser particles of gold settle, and coming in contact with the mercury surface of the copper plate, become superficially amalgamated and adhere to the mercury surface. After a sufficient time, which varies according to the amount of coarse gold in the ore, the stream of sludge is stopped and the table washed with water. The denser particles of pyrites, etc., which cover the table are scraped upwards from the bottom during the washing, to remove sand and slime. The pyrites or black sand as it is called, contains a considerable proportion of gold and is removed for separate treatment with mercury.

The amalgam is then scraped off the table, starting from the bottom upwards, by a steel amalgam scraper, collected for the recovery of the gold, and the plate reamalgamated.

The sludge, after passing the amalgamation tables, still contains a considerable proportion of finely divided gold in suspension, together with a little imperfectly crushed quartz which has escaped the mill screens. It is led by a main launder to the cyanide plant for further treatment, the sludge being hoisted to a higher level by means of a pump or

bucket wheel conveyer, so that in the subsequent operations, gravitation may be made use of as much as possible.

During the passage of the sludge over the main launder, it passes over a vessel in the shape of an inverted cone into which the heavy and imperfectly ground quartz falls, and is conveyed away by a pipe at the apex of the cone, to one or other of a series of tube mills, where it is reground, the fine sludge passing away from these mills being conducted back to the main launder. The sludge now contains the quartz in suspension partly as gritty sand and partly as fine slime.

The sands are usually treated for the recovery of gold by leaching methods, and for this treatment it is essential that they should be separated as far as possible from the accompanying slime, which would otherwise block the filtering surface and prevent the percolation of the solutions in the subsequent leaching operations. In order to accomplish this separation in an effective and simple manner, the sludge is made to flow over a receptacle built of light steel sheets in the shape of an inverted cone (conical classifier) or inverted pyramid as in the older types (spitzkasten) into which the sand falls while the liquor containing the slime passes on for separate treatment. The surface area of this trap must be of such a size that the flow of liquor is sufficiently retarded to allow the sand to settle. The sand passes away from the bottom of the collecting vessel by means of a hose or other distributing apparatus, into one or more of a series of tanks capable of holding 500 to 700 tons of wet sands. These tanks are fitted with a false bottom and filter of cocoanut matting, on the top of which are laid wood battens, two to three inches apart, to protect the filter surface from damage when the sands are emptied out of the tanks. Any slime which enters with the sands when the tank is being filled passes away with the excess water through adjustable gates fitted inside the tanks, which are gradually raised as the tank fills

with sand; or the tank is first filled with water, the slime then passing away with the displaced water at the periphery of the tank, where it is conducted to the slimes plant.

When the tank is sufficiently full of sand, the valve connected with the false bottom is opened, and the water allowed to drain away. This operation may take twelve hours or more, but may be accelerated by the application of a vacuum pump. When the sands are completely drained, leaching operations are commenced, and on to the wet sand, which usually contain from 10 to 15 per cent. of water, 100 to 120 tons of cyanide liquor of 0.1 to 0.15 per cent. sodium cyanide is added, allowed to stand some hours, and then drained off. The strength of the cyanide solution used depends on the nature of the ore, and also to a great extent on the individual fancy of the cyanide manager, but it rarely exceeds 0.25 per cent. and is seldom so strong. The sands are again washed with a further quantity of cyanide solution of a weaker strength, usually about 0.05 per cent. and finally with water to displace as much cyanide liquor as possible.

After each wash the water is drained away from the sands and left some time in order that air may penetrate far into the sands, and thus supply the oxygen so necessary for the solution of the gold in the cyanide liquor.

The slimes liquor after separation of the sands, is passed into a decantation vessel, allowed to settle, and as much clear liquor drained off as possible. Dilute cyanide solution is then added, the liquor agitated, and again allowed to settle and the clear cyanide solution decanted. This operation is repeated until all the gold has been dissolved and removed, which is usually accomplished in from two to three washes. The residual sludge is then either filter-pressed or run out into a dam, where any clear liquor that may further separate is pumped back into the cyanide system.

In order to obtain as complete a separation as possible the slime sludge is treated with a small portion of milk of lime added automatically before it enters the decantation system. This lime acts as a flocculating agent, and greatly assists the separation of clear liquor in the settling operations. Lime is also added to the cyanide solution, and besides the action above mentioned, it fulfils the important function of protective alkali, by combining with the carbon dioxide in the water, and absorbed from the air, to form insoluble calcium carbonate, and thus prevent the loss of active cyanide which would otherwise occur, by the liberation of hydrocyanic acid due to the action of the carbon dioxide on the alkaline cyanide :

$$2NaCN + H_2O + CO_2 = Na_2CO_3 + 2HCN.$$

In modern practice where fine grinding and efficient methods of separation are in operation, about 60 per cent. of sands, and 40 per cent. of slimes are obtained.

The gold-bearing solution, both from the sands and slimes treatment, is conducted to the precipitation house, where it is treated for the recovery of the gold. Before this treatment, however, it is usual to pass it through either a clarifying tank, or a filter-press, to remove any sediment or suspension.

The recovery treatment consists in passing the liquid through a series of boxes containing zinc shavings. These boxes are divided into compartments of about 130 cubic ft. capacity and the liquor which enters at the bottom of one compartment, slowly overflows at the top, and is conducted down to the bottom of the second compartment and so on. The liquid in its passage through the zinc boxes deposits practically all its gold contents on the zinc in the form of a finely divided black deposit, and passes into the sump where it is assayed for strength of free cyanide, and sufficient sodium cyanide added to bring the solution up to standard strength for a fresh operation.

If the liquor contains much organic matter it is sometimes clarified by the addition of potassium

permanganate before enriching with more cyanide, and it is usual to treat weak and strong liquor separately.

Other methods for the recovery of the gold from the cyanide solution have been proposed and used, such as the use of aluminium, nickel, etc., in place of zinc or by electrolysis, such as the electrolytic method of Siemens and Halska, but the process outlined above is the one generally adopted.

The zinc shavings are prepared by rolling thin sheets of zinc round a wooden mandril fixed in a lathe, and long ribbons of zinc turned off of about one five-hundredth of an inch thick. These turnings are dipped in a solution of lead acetate before placing in the zinc boxes, a thin deposit of lead being formed on the zinc surface which forms a lead zinc couple of greater gold precipitating efficiency than pure zinc.

Zinc dust or zinc ribbon prepared by the process of E. H. Strange, C. Pim and F. E. Matthews,[1] in which small jets of molten zinc are allowed to impinge on a rotating water-cooled drum, which instantly produces flattened zinc strips, have been proposed as substitutes for zinc shavings, but have not yet met with any great application. The most essential conditions for the efficiency of the zinc being the greatest zinc surface for the minimum weight of metal, a metal easily handled, and also that the surface shall be clean and bright, and free from oxide. These conditions are fulfilled to the greatest extent by the shavings obtained by turning down the roll of zinc sheets.

About once a fortnight, or such time as may be found necessary, a "clean up" in the extractor house takes place. The zinc boxes are unlocked, the zinc shavings taken out and washed on a screen, or by other means, to remove all adhering gold deposit, and the liquid pumped through a filter-press which has a sheet of filter-paper stretched over each cloth. When all the gold sludge has been filtered, the cake is washed with water, emptied out of the press, and digested in

[1] E.P. 7211 (1908).

a vat by agitation with dilute sulphuric acid; or better still with the cheaper and equally efficient sodium bisulphate. In this operation the small pieces of metallic zinc that have escaped the screen, and the zinc hydroxide and cyanide are dissolved. The residue is then again filter-pressed and washed, when a slimy black cake is obtained containing about 50 per cent. of moisture and 30 per cent. of gold, together with zinc ferrocyanide, silica and metallic impurities. The cake is then carefully calcined to drive off all water, and fused with a flux for the recovery of the bullion.

The zinc consumed in the process passes away partly as zinc sodium cyanide and zinc sodium ferrocyanide left in the treated material when thrown on the dump, and partly as zinc ferrocyanide, hydroxide and cyanide in the filtered gold slime. But the great bulk is converted into sulphate of zinc by the solution of small pieces of metallic zinc in the sulphuric acid in the treatment of the gold slime cake.

So far the efforts to recover the zinc have not been successful, the sulphate of zinc solution obtained on filtering the acid-treated gold slime generally being allowed to go to waste.

The consumption of cyanide has of late years been reduced to a minimum, about 0.4 lb. per ton of ore being an average consumption, but a small portion of this, however, actually takes part in the reaction of dissolving the gold, the remainder being converted into ferrocyanide, sodium zinc cyanide, thiocyanate and cyanate, and some lost through dissociation and evolution of hydrocyanic acid.

The cost of cyanide seldom amounts to more than fivepence per ton of ore treated, and is usually much lower. The total value of the cyanide consumed on the Rand in one year is now about £500,000 for the treatment of 25,000,000 tons of ore.

The salts remaining in the circulating liquor, such as the zinc sodium cyanide and sodium ferrocyanide, do not concentrate to any great extent, first because

a great deal of water becomes mixed with the liquor in each operation, and a considerable portion of the solution is left in the sands and slimes when thrown on the dump. And second, some of the zinc and ferrocyanide is deposited in an insoluble form partly in the sands and partly in the zinc boxes with the gold.

The water left wetting the sands would be anything from 15 per cent. to 10 per cent. in a well-drained tank, thus a tank holding 700 tons of drained sands with 10 per cent. of moisture would contain a total of seventy tons of water or nearly 16,000 gallons, which would be mixed with the first wash of 120 tons of cyanide liquor and therefore considerably dilute it.

Thus as a result of this dilution and the other causes mentioned above, the circulating liquor contains but a very small proportion of cyanogen compounds other than free cyanide.

The total cyanogen existing combined as cyanides and double cyanides in an average circulating liquor after passing the zinc boxes, would be about 0.1 per cent. calculated as potassium cyanide, of which not more than 0.004 is combined with zinc or iron. When the cyanide liquor is used in the stamp mill instead of water, the circulating liquor will, of course, become much more concentrated. Below is given an analysis made by the author of such a solution, although the practice of using cyanide solution in the mill is now seldom resorted to.

	Per cent.	Pts. per 100,000.
Sodium cyanide . .	0.03880	38.80
Sodium ferrocyanide .	0.00570	5.70
Sodium zinc cyanide .	0.04080	40.80
Sodium cuprocyanide .	0.00660	6.60
Sodium nickel cyanide .	0.00419	4.19
Sodium aurocyanide .	0.00091	0.91
Sodium cobalticyanide .	0.00290	2.90
Sodium cyanate . .	0.00780	7.80
Sodium thiocyanate .	0.01458	14.58

	Per cent.	Pts. per 100,000.
Sodium sulphate . .	0.16630	166.30
Sodium chloride . .	0.04614	46.14
Calcium sulphate . .	0.06600	66.00
Clacium hydroxide .	0.02440	24.40
Free ammonia . .	0.00136	1.36
	0.42648	426.48

The above description is roughly the general South African practice, but of course many variations in detail occur in individual mines; such, for example, as the use of vacuum filters for the removal of water from the sands; coarse grinding with the stamp mill and fine grinding by the aid of tube mills. And again at one time it was the practice, and is occasionally so now, to use cyanide solution in the mill instead of water. This practice, however, while greatly assisting the cyanide extraction by giving longer contact, seriously retards the amalgamation process and also dissolves some of the gold off the amalgamation plate. It can only be used with advantage when the proportion of coarse gold in the ore is low. Numerous other modifications are also in use, the description of which is, however, beyond the province of this book.

CHAPTER XIII

THE MANUFACTURE OF MERCURY FULMINATE

OF all the metallic fulminates the mercury salt is practically the only one that has received commercial application, most of the other salts being much too sensitive to shock to be of any practical value. Recently, however, the silver salt has been licensed for use, highly diluted, in the manufacture of caps for toy pistols. This salt is much more sensitive to shock or friction, and has greater explosive power than the mercury salt.

The processes in use to-day for the manufacture of mercury fulminate differ only in detail from that used by Liebig, and may be divided into two classes, viz. :

(1) Chavalier's modification of Liebig's process.
(2) Chandelon's process.

The latter is the one most generally adopted, while the former is sometimes used on the continent, principally in France. In both methods the same ingredients are used, and practically the same reactions occur. Metallic mercury is dissolved in nitric acid and then added to a large volume of ethyl alcohol, but whereas in Chavalier's process the mercury solution is added to the alcohol cold, in Chandelon's process it is added warm.

Chavalier's Process. One part by weight of mercury is dissolved in the cold in 10 parts of nitric acid of specific gravity of 1.3. When the mercury is completely dissolved the whole is poured into a vessel of large capacity (which should be 6 or 7 times the

volume of the total liquids) containing 6 parts of 90 per cent. alcohol.

After a short time a very vigorous reaction sets in, the liquid frothing considerably; the temperature may be reduced and the energy of the reaction retarded by the judicious addition of more alcohol, but care must be taken not to check the reaction too much or the product is liable to contain metallic mercury or other impurities.

Chandelon's Process. In this process the mercury is dissolved in a large amount of nitric acid, the mixture being heated during solution, and poured into the alcohol at a temperature of about 55° C. The reaction commences with energy, which may be checked as in the previous process, by the careful addition of a further quantity of alcohol, taking great care not to retard the action too much.

In both methods a considerable proportion of the alcohol volatilizes, and to prevent loss, the vessel is connected to an earthenware condenser which retains the alcohol and other volatile products which are driven off.

When the reaction is complete, the solution is cooled and the liquid filtered from the white or greyish-white mercury fulminate, which is thoroughly washed with water till quite free from acid.

The washed fulminate is usually stored under water in linen bags, in which condition it can be handled with comparative safety, for although mercury fulminate with from 5 to 30 per cent. of water may be exploded by blow or friction, the reaction is only confined to small patches, and is not communicated throughout the mass.[1]

When the fulminate is required in the dry state, it is spread out on trays made of a framework of wood with a strong net bottom and lined with linen or paper, which must contain no metal parts; the moisture is driven off by warm air, which must not exceed a temperature of 40° C. In the more modern

[1] Sprengstoffu Waffen u Munition (1909), 270.

practice vacuum driers are installed for drying the fulminate, which have the double advantage of drying the fulminate more efficiently and, owing to the vacuum, of preventing damage in case of explosion.

There are two commercial brands of fulminate on the market, viz., white and grey, but the product obtained by either of the two processes described above is usually of a brownish colour, and in order to obtain the white variety a small amount of metallic copper and hydrochloric acid is added to the acid solution of the mercury before adding to the alcohol. Salonina [1] recommends the addition of 2 per cent. cuprous chloride instead of hydrochloric acid and copper, as the latter is liable to cause the formation of oxalic acid: this addition yields a white fulminate free from metallic mercury.

The product may contain a considerable proportion of impurity formed in the course of manufacture. Mercury fulminate should be white or at most light grey, and should be practically completely soluble in ammonia, potassium cyanide solution, or concentrated hydrochloric acid. Metallic mercury which may be present is usually considered injurious.

Other methods for the technical production of fulminates have been proposed, but it is doubtful whether they have ever been applied on a manufacturing scale.

[1] *Zeitsch Ges. Schiess u Sprengstoffwesen* (1910), **41**, 67.

PART III

THE DETECTION AND ESTIMATION OF CYANOGEN COMPOUNDS

CHAPTER XIV

THE DETECTION AND ESTIMATION OF CYANIDES

HYDROCYANIC acid and the simple alkaline cyanides can be detected in solution by a number of well-known and characteristic reactions. If such a solution is made alkaline with caustic soda or potash, a little ferrous hydroxide added, and the mixture gently warmed, the cyanide is converted into ferrocyanide which may be recognized by acidifying the solution and adding a few drops of ferric chloride solution when a deep blue precipitate of prussian blue will be formed. If the cyanide solution is very dilute, the liquid to be tested must be made just alkaline with a 10 per cent. solution of caustic soda and evaporated gently nearly to dryness. It has been shown [1] that a very dilute solution of hydrocyanic acid may be treated in the manner described without suffering decomposition. To the nearly dry product is now added one drop of a 2 per cent. solution of ferrous

[1] G. D. Lauder and A. E. Walden, *Analyst* (1911), **36**, 266–70.

sulphate, and after ten to fifteen minutes two or three drops of hydrochloric acid, the whole is gently warmed and then cooled, and the presence of cyanide detected by the formation of a blue or bluish-green colour. This test is said to be exceedingly delicate.

A solution of an alkaline cyanide when mixed with a cold solution of sodium picrate, develops a dark coloration, which gradually deepens until after a time it becomes purple-red and opaque, the rate at which the colour develops is a rough guide as to the amount of cyanide present. If the test is applied to a 10 per cent. solution of potassium cyanide the colour develops after a few minutes ; with $\frac{1}{4}$ per cent. solution the colour is not fully developed until after standing two hours, but on greater dilution, such as one part in 1600 parts of water the liquid remains unchanged in colour for one hour, but after ten to twelve hours a perceptible and permanent colour is developed. The limit of the test is said to be 1 part of cyanide in 2000 parts of water. This test can only be used with advantage with the simple alkaline cyanides, silver or lead cyanide cannot be tested for by this method, zinc cyanide only in solution in ammonia or caustic soda, and cadmium and nickel cyanides only in caustic soda solution.[1] This test is stated by A. C. Chapman [2] to be unreliable, as a coloration may occur due to the formation of a salt of picramic acid by reducing agents.

An alkaline solution of phthalopherone has been proposed by Thieny [3] as a delicate test for a small quantity of hydrocyanic acid. The test solution is prepared by dissolving 0.5 grm. of phenolphthalein in 30 c.c. of absolute alcohol, water is added till a slight, permanent turbidity is produced; 20 grm. of caustic soda are then added, followed by powdered aluminium until the red colour of the solution

[1] G. Reichard, *Chem. Zeit.* (1901), **25**, 51, 537–38 ; *J.S.C.I.*, **20**, 935.

[2] *Analyst*, **35**, 469–77.

[3] *J. Pharm. Chem.* (1907), **25**, 51–53.

completely disappears. The solution is then diluted to 250 c.c. with oxygen, free distilled water, and filtered.

Strips of paper which have been dipped into a solution of sulphate of copper (0.05 per cent. $CuSO_4$). and dried, are moistened with the alkaline solution of phthalopherone prepared as above, and immersed in the suspected liquid. In the presence of hydrocyanic acid a red coloration is produced, which is permanent for twenty-four hours. Solutions containing persulphate, sodium peroxide or perborate also produce a red colour, which, however, is not permanent, but fades in a short time; hydrogen peroxide, ferric chloride or nitric acid are said not to yield any reaction.

Cyanides in a solid substance may be easily detected by conversion into thiocyanates by fusion with sodium thiosulphate. A small quantity of anhydrous sodium thiosulphate is fused in a test-tube, the substance to be tested then being added, and the mixture again heated for a short time. The fused mass is cooled, dissolved in a small quantity of water and a few drops of ferric chloride solution added. The formation of the deep red colour of ferric thiocyanate proves the presence of a cyanogen compound. Both the simple and complex double cyanides also yield this reaction.

Hydrocyanic acid may also be detected by the nitroferricyanide reaction; to the solution or distillate suspected to contain hydrocyanic acid is added a few pieces of sodium nitrite and two or three drops of ferric chloride solution, the brownish-red liquor which results is then acidified with dilute sulphuric acid drop by drop until the effervescence ceases and the liquid turns bright yellow. After heating to boiling the iron is precipitated by ammonia and the filtrate evaporated to dryness on the water-bath, redissolved in a little water and the solution cooled by ice. The addition of a drop of an alkaline sulphide solution produces a violet colour if hydrocyanic acid or a cyanide was originally present. This colour is not

stable, but rapidly passes first into blue, then green and finally yellow.[1]

A trace of a cyanide or hydrocyanic acid may be detected by warming the solution with a little tartaric acid, and allowing the vapour to react with a drop of ammonium sulphide on a watch-glass. The drop is carefully evaporated to dryness, dissolved in water and tested with a little ferric chloride. The development of a red colour, due to the formation of ferric thiocyanate, denotes the presence of a cyanide in the original liquor. It is said that this test may be applied in the presence of ferrocyanide, ferricyanide and thiocyanate, but it must be remembered in applying this test in the presence of ferrocyanides or ferricyanides that tartaric acid liberates free hydroferrocyanic and hydroferricyanic acids respectively, and that these acids readily decompose on warming yielding hydrocyanic acid.

Another test for hydrocyanic acid which is said to be exceedingly delicate, and to detect 1 part in 5,000,000, depends on the coloration produced when a cupric salt is added to a solution of hydrocyanic acid, containing an organic compound which forms a coloured oxidation product. The best substance for this purpose is said to be hydrocerulignone.[2]

ESTIMATION OF HYDROCYANIC ACID AND CYANIDES

Free hydrocyanic acid is much too weak an acid to be titrated with standard alkali, as no indicator is known that will record the end-point. The addition of mercuric chloride solution, however, liberates hydrochloric acid with formation of mercuric cyanide.

A method has been worked out based on this reaction

[1] H. J. van Giffen, *Pharm. Weekblad* (1910), **47**, 1043.
[2] J. Moir, *J.C.M.M.S., S.A.*, **10**, 342.

by Leopold Rosenthaler,[1] which is a modification of the method of Andrews.[2]

The solution which should not contain more than 1 per cent. of hydrocyanic acid, is treated with an excess of a neutral solution of mercuric chloride and sodium chloride—containing 22.1 gr. mercuric chloride and 11.7 grm. sodium chloride in 500 c.c.—and a few drops of a solution of iodoeosine, an indicator which is not affected by hydrocyanic acid, but is readily acted on by hydrochloric acid liberated by the reaction above mentioned according to the following equation :

$$2HCN + HgCl_2 = Hg(CN)_2 + 2HCl.$$

The solution is then titrated with standard N/10 alkali until the rose-red colour reappears : each c.c. of the alkali used is equivalent to 0.0027 grm. HCN.

Free hydrocyanic acid in presence of benzaldehydcyanhydrin may be estimated by taking say 10 c.c. of the solution and placing them in a separating funnel containing 20 c.c. of a neutral and saturated solution of sodium sulphate (to render the benzaldehydcyanhydrin practically insoluble), 50 c.c. of ether are then added, together with 10 drops of 0.2 per cent. alcoholic iodoeosin and the solution rendered neutral. Mercuric chloride solution is then added, the mixture well shaken and the aqueous liquor run off into a beaker containing distilled water, the funnel being rinsed with a little sulphate of sodium solution. This aqueous liquor which contains the liberated hydrochloric acid is titrated with N/10 alkali and the proportion of hydrocyanic acid calculated.[3]

The combined hydrocyanic acid of the benzaldehydcyanhydrin may be estimated together with the free hydrocyanic acid by treating a measured quantity of the liquor with a few drops of the iodoeosine indicator, and an excess of N/10 caustic potash solution, of sufficient quantity to maintain the rose-red colour

[1] *Arch. Pharm.* (1910), **248**, 529–33.
[2] *J.C.S.* (1903), ii. 695.
[3] L. Rosenthaler, *J.C.S.* (1910), ii. 1119.

of the indicator after the addition of the mercuric chloride solution and vigorous shaking, the liquid being then neutralized with N/10 sulphuric acid. The number of c.c. of N/10 sulphuric acid used subtracted from the number of c.c. of N/10 caustic potash originally added will yield the amount of alkali neutralized by the liberated hydrochloric acid. These reactions may be expressed thus :

1. $HCN + KOH = KCN + H_2O$.
2. $KOH + CHPhOH.CN = KCN + PhCHO + H_2O$.
3. $2KCN + HgCl_2 = Hg(CN)_2 + 2KCl$.

The estimation of free hydrocyanic acid in Cherry Laurel water by means of a solution of sulphate of copper in excess of ammonia (Burquel's process) is open to the well-known objection of the difficulty of determining the final end-point. G. Guerin and L. Gouet [1] suggested to overcome this difficulty the addition of sodium sulphate ; 25 c.c. of the cherry laurel water are diluted to 100 c.c., and 20 drops of caustic soda solution added, followed by 10 c.c. of ammonia and 0.5 grm. of sodium sulphate, the mixture being then titrated with a standard solution of copper sulphate of such strength that 1 c.c. is equivalent to 0.01 grm. of hydrocyanic acid, until a faint blue tinge appears. The addition of caustic soda is in order to prevent the formation of hydrobenzamide. When this method is used to estimate hydrocyanic acid in dilute solutions the addition of the caustic soda is not necessary.

Small quantities of hydrocyanic acid or cyanides may be estimated [2] by conversion into prussian blue and matching the blue suspension in a colorimeter with a prepared standard. By this method it is said to be possible to estimate 0.004 to 0.0004 grm. of hydrocyanic acid per 1 c.c. The solution is made strongly alkaline with caustic soda or potash followed by a dilute solution of ferrous sulphate, well shaken

[1] *J. Pharm. Chim.* (1909), **29**, 234–36.
[2] *Ber.*, **43**, 1430–31.

and then boiled for ten minutes, cooled and just acidified with hydrochloric acid. After standing for some time a precipitate of prussian blue is gradually formed, when the whole liquid is diluted to 100 c.c. and matched with a standard blue colour made from a known quantity of pure potassium ferrocyanide.

Should the original liquid be strongly coloured, the blue precipitate must be allowed to settle, and the clear liquor decanted off and replaced by distilled water.

If the cyanide is very dilute it may first be acidified with hydrochloric acid, and the liberated hydrocyanic acid extracted with ether; the resulting ethereal solution is then shaken with a small quantity of caustic potash solution and treated in the manner above described.

Small quantities of cyanide may also be estimated colorimetrically by the action of an alkaline picrate, but as has been pointed out by A. C. Chapman,[1] the product formed when a solution of an alkaline picrate acts on a cyanide is either isopurpurate of potassium or the alkaline salt of nitroamine phenol; the former is formed when the cyanide is in excess, and the latter in the presence of excess of picrate. In testing for small quantities of cyanide nitroamine phenol is the product as the picrate is usually in excess and this body is formed as the result of the reduction of the picric acid by the cyanide. This test, however, has a very limited value as certain other bodies also reduce the picrate, such as acetone, aldehyde or hydrogen sulphide.[2]

ESTIMATION OF CYANIDES

The methods usually adopted for the estimation of soluble alkaline cyanides are founded on the precipitation of argentic cyanide.

Determination as Silver Cyanide Gravimetrically. To the solution containing free hydrocyanic acid, or the cyanides of the alkali or alkaline earth metals diluted

[1] *Analyst* (1910), **35**, 469–75.
[2] *J.C.S.* (1910), ii. 1119.

to a convenient volume with distilled water, add an excess of silver nitrate and then acidify the liquid with dilute nitric acid. Allow the precipitate to settle, which may be greatly accelerated by first rapidly agitating the liquid, and then filter on a tarred filter and wash and dry at 100° C., and weigh as AgCN. No heat must be applied until after the precipitate has been filtered and washed. If the silver cyanide is ignited in an open dish in contact with the air, at a red heat for fifteen to twenty minutes, the silver cyanide is reduced to metallic silver which may be weighed as such, and the weight of metallic silver divided by four will represent the amount of hydrocyanic acid originally precipitated.

This method is of course only applicable in the absence of any impurity capable of forming an insoluble salt with silver in a dilute nitric acid solution.

Sulphides can be removed before the addition of silver nitrate by shaking the liquid with freshly precipitated lead carbonate or lead sulphate and filtering off the lead sulphide.

In the presence of chlorides, bromides or iodides the precipitated silver cyanide will be contaminated by the silver salts of these elements, but if the mixed precipitates are boiled with a solution of mercuric oxide in acetic acid—prepared by warming freshly precipitated mercuric oxide in dilute acetic acid—the silver cyanide is decomposed with formation of silver acetate and mercuric cyanide :

$$Hg(C_2H_3O)_2 + 2AgCN = Hg(CN)_2 + 2AgC_2H_3O.$$

On filtering the solution and washing the precipitate, the silver may be determined as silver chloride or as metallic silver; the latter method is preferable owing to the difficulty of preventing the silver chloride from carrying down some of the mercury with it, the reduction being accomplished by heating in a current of hydrogen.

A more simple method than the above of separating the cyanide, and one equally as accurate, is to distil

the cyanide solution with acetic acid and to determine the hydrocyanic acid in the distillate, and the chlorine in the acid residue.

Volumetric Determination by Silver Solution. This method, which was originally proposed by Liebig, has been subsequently modified by a number of investigators, and is the one usually adopted in practice for the rapid estimation of cyanides. It is equally as accurate as the preceding, and has the added advantage of speed.

This method is based on the fact that silver forms a soluble double salt with the alkaline cyanide thus :

$$2NaCN + AgNO_3 = NaAg(CN)_2 + NaNO_3.$$

When the whole of the cyanide has been converted into the double salt, any further addition of the silver solution produces a permanent opalescent turbidity due to the precipitation of silver cyanide. The first appearance of this opalescence indicates the end-point of the above reaction.

In carrying out the method a solution of cyanide is taken containing about 0.1 to 0.15 grm. HCN. Any free hydrocyanic acid being first neutralized with sodium or potassium hydroxide avoiding excess, a few drops of a 10 per cent. solution of potassium iodide added, and then decinormal silver nitrate solution run slowly into the liquid from a burette, agitating the liquid the while, until the first appearance of an opalescence which remains permanent on agitating and standing. The first appearance of this opalescence can be more readily observed if the liquid is viewed with a black background. The end-point is exceedingly sharp and easily observed, the silver solution being added rapidly at first and then more and more slowly as the precipitates which at first forms as the silver solution enters the cyanide liquor, dissolves more sluggishly.

The haloid salts do not interfere with this reaction, but sulphides, excess of caustic alkalis or free ammonia should be avoided, the latter body yielding much too high a result. The addition of a little potassium iodide is necessary, not only because it renders the

end-point sharper and more distinct, but it prevents the high readings that would otherwise take place in the presence of certain salts such as the ferrocyanides, caustic alkalis, etc.

Hydrocyanic acid may be estimated separately in the presence of alkaline cyanides by first adding the standard silver solution to a measured volume of the cyanide liquor without any other addition than a few drops of a 10 per cent. solution of potassium iodide in the manner already described. And then estimating the total cyanide by the silver nitrate after the addition of caustic soda solution in sufficient quantities to neutralize the free hydrocyanic acid, and a few drops of potassium iodide solution. The results obtained from the first estimation represent the silver solution required for the alkaline cyanide only, and the second that required for the alkaline cyanide plus the hydrocyanic acid. By deducting the first reading from the second a figure is obtained corresponding to the amount of free hydrocyanic acid in solution.

One c.c. of decinormal silver nitrate solution is equivalent to 0.0054 HCN, 0.01302 KCN or 0.0098 NaCN.

For the estimation of dilute cyanide solutions, N/100 silver nitrate solution may be used.

The alkaline cyanides when combined with the cyanides of heavy metals forming simple double cyanides such as those of zinc, nickel, copper, etc.—are, of course, not estimated by the silver process, but after the addition of excess of caustic soda or potash the whole of the cyanogen combined as a double zinc or cadmium cyanide may be estimated by the silver solution. The caustic alkali has no influence on the accuracy of the end-point if potassium iodide is used as an indicator, the action of the alkali being to form an alkaline cyanide and a zincate :

$$K_2Zn(CN)_4 + 4KOH = 4KCN + K_2Zn(OH)_4.$$

In the process suggested by Hanway,[1] a standard

[1] *J.C.S.*, ~~95~~ 245.

solution of mercuric chloride is substituted for the silver solution in Liebig's method, and is based on the property of mercury salts of at once forming mercuric cyanide when added to a solution of an alkaline cyanide.

A known volume of the cyanide solution to be tested is taken and made alkaline with ammonia in slight excess and then decinormal mercuric chloride solution (13.55 grm. $HgCl_2$ per litre) is gradually added from a burette, agitating the liquid after each addition until a permanent opalescence is observed, that does not disappear on shaking, as in the titration with silver salts.

Alkaline sulphides, chlorides, carbonates or hydroxides do not interfere with the process nor do thiocyanates or cyanates. The double cyanides of silver, zinc, nickel, etc., are also decomposed by the mercury solution, so that these simple double cyanides, if they exist in the liquor, are estimated along with the alkaline cyanide.

This method is useful for the determination of the total cyanogen in the alkaline cyanides and simple double cyanides in electroplating liquor, and the dilute cyanide solution used in gold-mining operations.

The reaction of the mercury salt with the cyanide can be expressed as follows :

$$2KCN + HgCl_2 = Hg(CN)_2 + 2KCl.$$
$$K_2Zn(CN)_4 + 2HgCl_2 = 2Hg(CN)_2 + 2KCl + ZnCl_2.$$

each cubic centimetre of the decinormal mercuric solution is equivalent to 0.00651KCN ; or 0.0049NaCN; or 0.0027HCN.

The cyanide combined as a double cyanide of copper may also be estimated by this method if an excess of ferrocyanide is added.

The use of a standard solution of mercurous nitrate for the estimation of cyanides has been proposed by Cohen [1] and worked out by Ruff and Krauss and others, and has been found to give good results with

[1] *J.C.S.* (1902), ii. 50.

hydrocyanic acid alone or in the presence of benzaldehydcyanhydrin, cyanides, bromides and iodides.[1]

If potassium mercuric iodide is used as an indicator, the end-point is shown by the appearance of a scarlet precipitate ; caustic alkalis if present should, however, be first neutralized by the addition of sodium hydrogen carbonate.

Determination by a Standard Nickel Solution. This method is also exceedingly similar to Liebig's method, and is carried out in like manner. To a solution of the cyanide is gradually added a standard solution of a nickel salt until the appearance of a permanent opalescence due to the separation of the apple-green cyanide of nickel. The appearance of this turbidity marks the end-point of the reaction.

A standard solution is prepared by dissolving 35.105 grm. of crystallized sulphate of nickel in 1000 c.c. of water, the solution is poured into a burette and run into a measured quantity of the cyanide solution to be estimated until the appearance of the turbidity. By adding to the liquid 5 to 10 drops of ammonia the end-point is rendered much sharper by rapidly redissolving the nickel cyanide which at first forms, at the point where the nickel solution first enters the liquid, whereas without this addition the nickel cyanide dissolves very slowly on agitation.

The action of the nickel solution on the cyanide is represented by the equation :

$$4KCN + NiSO_4 = K_2Ni(CN)_4 + K_2SO_4.$$

And any nickel solution added after the completion of the above reaction produces a permanent precipitate of nickel cyanide. Each cubic centimetre of the nickel solution corresponds to 0.03255KCN.

Neither chlorides, bromides, iodides or thiocyanates interfere with this reaction as the nickel compounds of these salts are all soluble. This, however, does not give this process any advantage over Liebig's silver method

[1] L. Rosenthaler, *Arch. Pharm.* (1911), **249**, 253–59 ; *J.C.S.* (1911), ii. 668.

as these salts do not interfere with the latter process if potassium iodide is used as an indicator.

Estimation by Means of Standard Iodine Solution. The addition of iodine to a solution of a cyanide produces potassium iodide and cyanogen iodide, and the end of the reaction is indicated by the yellow tint produced by the excess of iodine. This point may be rendered more sharply marked by the addition of starch paste, but caustic alkalis, sulphides, carbonates and reducing agents generally should be absent.

The reaction may be expressed thus :

$$I_2 + KCN = KI + CNI.$$

Cyanogen existing in combination with zinc may be estimated together with the free cyanide by modifying the above process by adding an excess of sodium or potassium ferrocyanide to a solution of the mixed cyanides, after neutralization of any excess alkali that may be present, and then titrating the solution with standard iodine.

The reaction that takes place may be expressed by the equation :

$$3K_2Zn(CN)_4 + 2K_4Fe(CN)_6 + 12I_2 = Zn_3K_2[Fe(CN)_6]_2 + 12KI + 12CNI.$$

The cyanogen combined with the simple double cyanides such as those of zinc, silver or mercury may be estimated by first precipitating the heavy metal as sulphide by the addition of sufficient sodium sulphide, and removing the excess of sulphide by shaking the liquor with the carbonate or sulphate of lead. The cyanide in the filtered solution may then be titrated either with the iodine solution as described above or by standard silver nitrate solution. By warming the solution the precipitation of the metals as sulphides is rendered more complete. Copper and nickel, however, are not removed from a double cyanide by this method.

Another volumetric method for the estimation of cyanides has been described in which use is made of a

standard solution of a cupric salt. This method differs somewhat from those previously described in that the end-point is determined by the appearance of a blue colour and not the formation of a turbidity. It is merely a reversal of the well-known method for the estimation of copper by a cyanide solution.

A portion of the alkaline cyanide solution is made strongly alkaline with ammonia and a standard solution of sulphate of copper run in gradually from a burette with agitation, until the first sign of the appearance of the blue colour due to the solution of copper oxide in ammonia.

This method has no advantage over those already described, and has the objection that the end-point is somewhat indefinite. It is also upset by the presence of certain other bodies such as the double cyanides of zinc and excess of ammonium salts.

ESTIMATION OF THE CYANOGEN IN SLIGHTLY DISSOCIATED SALTS

Certain cyanides which dissociate in solution but slightly, such as mercury cyanide, cannot be estimated by Liebig's method as no precipitate of silver cyanide is produced when silver nitrate solution is added to a solution of mercuric cyanide.

If, however, the solution of mercuric cyanide is shaken with aluminium powder, the filtered liquid can then be titrated by Liebig's method.[1] The solution is first made alkaline with caustic soda or potash solution and then aluminium powder gradually added, the liquid being well shaken after each addition; as the aluminium dissolves the mercury is precipitated. When the whole of the mercury is deposited the solution is filtered, a few drops of a 10 per cent. solution of potassium iodide added, and the cyanogen estimated by titration with decinormal silver nitrate until the appearance of a permanent turbidity.

[1] Virconzo Borcelli, *Gazz.* (1907), 371, 429–34; *J.C.S.*, ii. 825 (1907).

This method can also be applied to any of the complex iron cyanogen compounds by first converting them into mercuric cyanide by boiling with an excess of mercuric oxide and proceeding as described above with the filtered solution.

Mercuric cyanide may, however, be directly estimated by Forde and Gelis' method without the necessity of first removing the mercury as metal or as sulphide, by taking a dilute solution of the salt and titrating with standard iodine solution when the following reaction takes place :

$$Hg(CN)_2 + 2I_2 = HgI_2 + 2CNI.$$

Take 0.1 grm. of the cyanide and dissolve in 400 to 500 c.c. of distilled water or a known volume of the solution containing an equivalent quantity of the cyanide diluted to the same bulk and then titrate with the N/10 iodine solution. Any precipitate of mercuric iodide that may occur must be brought into solution by the addition of sufficient potassium iodide.

ESTIMATION OF CYANIDE IN PRESENCE OF FERROCYANIDES

This separation may be readily accomplished by the method proposed by W. Feld, which is based on the fact that in certain cyanides such as those of lead and magnesium, the cyanogen is very weakly held, and that when these cyanides are boiled with water, the whole of the cyanogen is quantitatively expelled as hydrocyanic acid with the steam. Thus when alkaline cyanides are boiled with solutions of these salts, hydrocyanic acid is evolved according to the reaction :

$$MgCl_2 + 2KCN + 2H_2O = Mg(OH)_2 + 2HCN + 2KCl.$$

A known weight of the cyanide or a measured volume of the solution containing about 0.25 to 0.5 grm. of cyanide is diluted to 100 c.c. with water and distilled with 300 c.c. of N/– magnesium chloride solution for fifteen to twenty minutes, the steam

containing the hydrocyanic acid being passed through a condenser into a dilute solution of caustic soda or potash, and the cyanide solution so obtained titrated with standard silver solution.

If sulphides are present in the original solution, they will be decomposed by the magnesium chloride in the same manner as the cyanide :

$$K_2S + MgCl_2 + 2H_2O = Mg(OH)_2 + H_2S + 2KCl.$$

The hydrogen sulphide will pass over into the condenser along with the hydrocyanic acid and will interfere with the estimation of the cyanide. To remedy this, lead nitrate is substituted for the magnesium chloride ; only hydrocyanic is then evolved, all the sulphide being left behind in the still as the black insoluble lead sulphide :

$$K_2S + 2KCN + 2Pb(NO_3)_2 + 2H_2O = PbS + Pb(OH)_2 + 2HCN + 4KNO_3.$$

Another method for the estimation of cyanides in the presence of ferrocyanides is to pass an excess of carbon dioxide through the solution and to absorb the evolved hydrocyanic acid in alkali. The accuracy of this method is, however, open to some doubt, as small portions of the ferrocyanide would be decomposed by this treatment, the following reaction being known to take place to a limited extent under these conditions :

$$2K_4Fe(CN)_6 + 3H_2O + 3CO_2 = FeK_2Fe(CN)_6 + 6HCN + 3K_2CO_3.$$

If however the solution is distilled with excess of sodium bicarbonate the ferrocyanide would be unattacked, but all the cyanide decomposed and the hydrocyanic acid driven off which may be absorbed in a caustic alkali solution, and estimated in the usual manner.

THE ANALYSIS OF COMMERCIAL CYANIDE

In the examination of commercial cyanide it is generally necessary to know not only the amount of alkaline cyanide present, but the nature and extent of the impurities, and the sample should be examined for cyanate, carbonate, hydroxide, chloride, cyanamide, formate, ferrocyanide, sulphide, silicate and thiocyanate as well as for cyanide.

Owing to the common practice of the trade in calculating all cyanide in terms of potassium cyanide, a sample of cyanide of 98 to 100 per cent., but containing say 40 per cent. sodium cyanide would also contain 12 to 13 per cent. of impurities thus :

Actual Contents.		Calculated according to Trade Methods.	
Sodium cyanide	= 40.0	Calculated as potassium cyanide	= 52.7
Potassium cyanide	= 47.3	Calculated as potassium cyanide	= 47.3
Total weight of sodium and potassium cyanide	= 87.3	Total cyanide calculated as potassium cyanide	100.00
Impurities	= 12.7		
	100.00		

Five grams of the sample should be carefully weighed out, dissolved in distilled water and diluted to 1000 c.c.

Estimation of Cyanide. Take 50 c.c. of the solution prepared as above, transfer to a beaker flask, dilute with distilled water, then add a few drops of potassium iodide indicator, and titrate with decinormal silver nitrate solution until the appearance of a faint but permanent opalescence as described under cyanide estimation. If the cyanide contains sulphide it must be removed before the cyanide estimation is made. This is readily accomplished by shaking up the cyanide solution with some pure freshly precipitated lead

carbonate or sulphate, and then filtering the purified cyanide solution from the lead sulphide.

The above method for estimating the cyanide is by far the simplest and most rapid method, but if it is desired to estimate the cyanide gravimetrically, then an excess of silver nitrate solution must be added to 50 c.c. of the diluted cyanide solution rendered just acid with nitric acid, and the insoluble cyanide filtered and thoroughly washed. This precipitate will contain any chloride that may exist in the sample. Wash the precipitate out into a beaker and boil with a solution of mercuric acetate when the silver cyanide will be decomposed into silver acetate with formation of mercuric cyanide, both of which are soluble and pass into solution, filter from any undecomposed silver chloride, and estimate the silver in solution either by titration with N/10 sodium chloride or by precipitation as chloride and weighing the washed and dried precipitate as silver chloride or as metallic silver after reduction of the chloride in a current of hydrogen.

Estimation of Chloride. Take 50 c.c. of the solution, transfer to a distilling flask and dilute to 100 to 150 c.c., then acidify with a slight excess of acetic acid and distil. By this means the whole of the cyanide will be decomposed and the hydrocyanic acid driven off with the steam, which on account of its poisonous nature should be passed through a condenser and absorbed in caustic soda solution. When the whole of the hydrocyanic acid has been driven off, the distillation is stopped and the liquor washed out of the distilling flask into a beaker, and precipitated with excess of silver nitrate solution. After agitating the solution to clot the precipitate together it is filtered off, washed and dried at 100° C. and estimated as AgCl or as metallic silver after reduction in a current of hydrogen. A more rapid and quite as satisfactory a method is to estimate the chlorine volumetrically with standard decinormal silver nitrate solution. This is best performed by first neutralizing the free acetic acid in the liquid washed out of the flask with an excess of

ammonia and evaporated to dryness in a porcelain dish on the water-bath to drive off all excess of free ammonia. The residue is then redissolved in a little distilled water, and keeping the solution in the white dish, and after adding a few drops of potassium chromate indicator it is titrated slowly, drop by drop, with a solution of N/10 silver nitrate from a burette until the faint brick-red colour of silver chromate remains permanent on agitation. One c.c. of N/10 $AgNO_3$ = .00354 grm. Cl or 0.00584 grm. NaCl.

Another method of rapidly estimating the chloride in solution is to add to 50 c.c. of the cyanide liquor after dilution an excess of a pure solution of zinc sulphate free from chloride. This will precipitate the hydroxide, cyanide, carbonate and ferrocyanide. Dilute the mixture to a definite volume, filter and titrate an aliquot part with N/10 silver nitrate solution after the addition of a few drops of the potassium chromate indicator. This method is only accurate in the known absence of cyanate and thiocyanate.

The chloride may also be rapidly determined by the method of Karl Polstorff and H. Meyer,[1] which depends on the fact that hydrocyanic acid in dilute solutions combines with formaldehyde, forming a compound not precipitable by silver nitrate.

To 100 c.c. of the cyanide solution (containing 0.5 grm. of the sample) made alkaline with sodium hydroxide if necessary, add 20 to 30 drops of 35 per cent. formaldehyde solution.

After a few minutes 5 c.c. of strong nitric acid are added, and the chloride titrated with standard silver nitrate solution.

If the amount of chloride present is very small, a larger proportion of the cyanide solution should be taken and N/100 substituted for the N/10 silver nitrate solution.

Estimation of Carbonate. Take 100 c.c. of the cyanide solution, transfer to a beaker and add an excess of barium or calcium nitrate solution. The

[1] *Z. Anal. Chem.* (1912) **51**, 601–9.

alkaline carbonate is then precipitated as calcium or barium carbonate. Allow the precipitate to settle for an hour or so out of air contact, and in the cold, then filter and wash, keeping the air away as much as possible. The insoluble carbonates may then be titrated with N/10 nitric acid, using methyl orange as indicator. One cubic centimetre of $N/10HNO_3$ = .0053 grm. sodium carbonate or 0.0069 potassium carbonate.

Estimation of Alkaline Hydroxide. Free alkaline hydroxide may be estimated by the method described by Clenell.[1] To 50 or 100 c.c. of the cyanide solution standard silver nitrate solution is run in to the point of faint but permanent opalescence and then the free alkali titrated with standard acid, using phenolphthalein as indicator. From the result must be deducted the equivalent due to alkaline carbonate, bearing in mind the fact that when using phenolphthalein alkaline carbonates are indicated only to the point of half neutralization thus :

$$2Na_2CO_3 + H_2SO_4 = 2NaHCO_3 + Na_2SO_4.$$

bicarbonate of sodium being neutral to phenolphthalein. Thus 1 c.c. of N/10 sulphuric acid when using this indicator is equivalent to 0.004 grm. of sodium hydroxide, but 0.0106 of sodium carbonate.

The hydroxide may also be estimated together with the carbonate by taking 50 c.c. of the solution, diluting to 200 c.c. with distilled water and adding a known volume of standard sulphuric acid sufficient to neutralize completely both the hydroxide and carbonate and to liberate a little free hydrocyanic acid from the cyanide ; immediately after the addition of the standard acid an excess of neutral mercuric chloride solution is added, and the free hydrochloric acid liberated according to the equation :

$$2HCN + H_2Cl_2 = Hg(CN)_2 + 2HCl.$$

[1] *Chem. News*, vol. 71, p. 93 ; *Chem. Cy. Sol.*, p. 63.

may then be titrated with standard alkali. The excess acid thus found together with the acid required for the carbonate deducted from the acid, originally added, will yield the acid equivalent of the hydroxide.

Very accurate results may be obtained by the method of A. Schland, who prepares a standard solution of soluble prussian blue by adding ferric chloride to a large excess of potassium ferrocyanide, then washing the precipitate by decantation as far as possible. It is diluted to a definite bulk and standardized against a standard alkaline hydroxide solution.

A known volume of the cyanide solution is titrated with silver nitrate to a faint opalescence to convert all free cyanide into the stable double silver cyanide, and then with a solution of barium nitrate to remove all soluble carbonate. The resulting filtered solution is warmed to 30° to 40° C. and titrated with the standard prussian blue suspension which, of course, must be well shaken before use, until a slight blue colour remains permanent.[1]

Estimation of Cyanate. Cyanates may be easily and readily detected in cyanide by taking 3 to 5 grm. of the cyanide, dissolving it in the smallest possible quantity of water, an excess of carbon dioxide is passed through the solution until all the cyanide is decomposed and the hydrocyanic acid evolved, 95 per cent. alcohol is then added to precipitate the carbonate and bicarbonate and the liquid filtered. The filtrate is then just acidified with acetic acid and a solution of cobalt acetate added. If any cyanate is present a deep blue colour is produced due to the formation of the double potassic cobaltic cyanate.

Undoubtedly the best method for the determination of cyanates is based on the decomposition which these salts undergo when warmed in aqueous solutions with mineral acids, with formation of ammonia and carbon dioxide :

$$HCNO + H_2O = NH_3 + CO_2.$$

Acidify 100 c.c. of the cyanide solution with dilute

[1] *Thorp's Dict. App. Chem.* (1910), vol. i.

sulphuric or hydrochloric acid and boil under a hood in a draught cupboard ; by this means the whole of the nitrogen combined as cyanide is driven off with the steam of the boiling water as hydrocyanic acid, while the cyanate is decomposed into carbon dioxide and ammonia, the latter compound being fixed by the excess acid as an ammonium salt. When the whole of the hydrocyanic acid has been driven off, the acid liquor is washed into a distilling flask, neutralized with an excess of caustic soda solution, and distilled, the vapour containing the ammonia being conducted through a condenser into a measured quantity of N/10 sulphuric acid. When the whole of the ammonia is distilled over the excess of acid is titrated back with N/10 alkali. The amount of acid consumed is a direct measure of the cyanate present, 1 c.c. of N/10 sulphuric acid being equivalent to 0.0081 grm. KCNO or 0.0065 NaCNO.

Estimation of Sulphide. Sulphide in cyanides may be estimated by first shaking the solution with lead carbonate and oxidizing the filtered lead sulphide to sulphate, and estimating the latter in the usual manner.

To 50 c.c. of the cyanide solution add an excess of pure and freshly precipitated lead carbonate and agitate well, filter off the blackened lead precipitate and thoroughly wash, then transfer out of the filter-paper into a dish and evaporate to dryness with strong nitric acid. The residue is redissolved in a little water and the sulphate of lead filtered off and weighed.

Colorimetric determination of small quantities of sulphides in cyanides, by matching the colour produced by the addition of sodium nitroprussiate, with a standard, has been proposed by J. Loevy.[1]

To carry out this method the following three solutions are required :

1. A solution of 40 grm. of crystallized sodium sulphide in 1000 c.c. of distilled water, made slightly alkaline to preserve the sulphide : 1 c.c. of this solution should contain 0.0053 grm. of sulphur.

[1] *J.C.M.M.S., S.A.* (1899), [2], 54, 55.

2. A solution of 44.15 grm. of crystallized sulphate of zinc in 1000 c.c. of water. 1 c.c. = 0.01 grm. zinc.

3. A solution of sodium nitro prussiate to which a few drops of a 5 per cent. potassium cyanide solution has been added.

The sulphide solution is accurately standardized by means of the zinc solution.

The estimation is made by placing the cyanide solution to be tested in one cylinder and a pure cyanide solution of equal volume in another, and to each is added 1 c.c. of the nitroprussiate solution.

If the cyanide solution in the first cylinder contains sulphide the characteristic red-violet colour will be developed which is then matched by adding the standard sodium sulphide solution (previously diluted 1 to 10) to the pure cyanide in the second cylinder.

The limits for this method are stated to be between 0.0005 and 0.0015 per cent. of sulphur in the solution, and the coloration within these limits will last ten to thirty minutes. If below the limit it is indistinct and disappears too rapidly, and if above it is too dark and the solution must be diluted.

Clenell [1] has described a method for the estimation of sulphide in cyanide, based on the reaction which takes place when a soluble sulphide is added to a solution of sodium or potassium silver cyanide. A portion of the cyanide solution is shaken with lead carbonate and filtered to remove all sulphide, and then carefully titrated with N/10 silver nitrate solution in the usual manner. To a second and equal portion of the cyanide solution, sodic silver cyanide solution is added in excess, which reacts with the soluble sulphide producing an equivalent quantity of free sodium cyanide thus :

$$2NaAg(CN)_2 + Na_2S = Ag_2S + 4NaCN.$$

The black silver sulphide is filtered off and thoroughly washed and the cyanide in the filtrate determined by the standard silver solution and the number of c.c.

[1] *Chem. of Cyanide Sol.*, p. 93.

of silver solution used in the first titration deducted. The remainder will be the cyanide equivalent of the sulphide originally present in solution and each cubic centimetre of the silver solution used in excess is equivalent to 0.0016 of sulphur or 0.0039 sodium sulphide.

In the method of Feldtmann and Bettel [1] the sulphur is separated from the cyanide solution by agitation with pure lead carbonate, and the filtered and washed lead sulphide digested in a solution of pure sodium cyanide containing hydrogen peroxide, which converts the sulphur into thiocyanate, the latter being estimated in the usual manner.

T. Ewan [2] has worked out a modification of the lead method which is applicable for the determination of small quantities of sulphides : 10 grm. of the sample are dissolved in a small quantity of water and titrated with a standard lead nitrate solution until a drop of the solution on a filter-paper ceases to produce a colour with a drop of lead solution. These results are, however, too low, owing to the oxidation due to dissolved oxygen in the water used, and it is suggested that for small quantities of sulphides results sufficiently correct for practical purposes may be obtained by multiplying the result by 1.25 or by dissolving 2.4 grm. of pure dry lead nitrate in 1000 c.c. of water and taking 1 c.c. as equivalent to 0.01 per cent. K_2S, in the cyanide.

According to E. C. Rossiter,[3] the most satisfactory method for the estimation of sulphide in cyanide is by a modification of the lead nitrate method. First the sulphide is determined by Ewan's method, then 100 grm. of the cyanide are dissolved in air-free water and a weighed quantity of pure lead nitrate which has been dried over sulphuric added sufficient to precipitate all the sulphide present plus 10 per cent. The excess of lead nitrate is then estimated by titration with a standard solution of sodium sulphide

[1] *J.C.M.M.S., S.A.*, vol. i. 267–73.
[2] *J.S.C.I.*, **28**, 10–3. [3] *J.S.C.I.*, **30**, 583–88.

which has been previously standardized with N/10 iodine solution. It is stated that this method will determine 1 part of sulphur in 100,000 parts of the cyanide.

SEPARATION AND ESTIMATION OF HYDROCYANIC ACID IN PRESENCE OF CYANOGEN

This separation is readily accomplished by the method proposed by F. Rhodes,[1] which depends on the fact that hydrocyanic acid is absorbed by a solution of silver nitrate with precipitation of silver cyanide while the cyanogen is unabsorbed.

The mixed gases are therefore passed through two absorption tubes, the first containing 10 c.c. of a 10 per cent. solution of silver nitrate just acidified with a drop of dilute nitric acid, while the other contains 10 c.c. of a seminormal potassium hydroxide solution.

All the hydrocyanic acid is absorbed by the silver nitrate in the first tube and precipitated as silver cyanide, which may be filtered, washed and estimated in the usual manner. The cyanogen which passes through the first tube unchanged is absorbed in the alkaline solution in the second tube as cyanide and cyanate, which may be estimated by N/100 silver solution, 1 c.c. of which is equivalent to 0.00104 cyanogen.

[1] *J. Ind. Eng. Chem.* (1912), **4**, 652–55.

CHAPTER XV

ESTIMATION OF FERROCYANIDE

A VARIETY of methods have been proposed from time to time for the estimation of ferrocyanides, all more or less accurate. They may be classed under the following heads, viz. :

1. Estimation of the total nitrogen as ammonia, by Kjeldahl's method.
2. Estimation of the ferrocyanogen iron by ignition with concentrated sulphuric acid.
3. Precipitation of the ferric salt and determination of the ferric oxide in the ash, after ignition in air, of the washed and dried product.
4. Oxidation of the ferrocyanide to ferricyanide by suitable oxidizing agents.
5. Titration of the ferrocyanide solution with standard solutions of the heavy metals.
6. Estimation of the total cyanogen as an alkaline cyanide, after first decomposing the ferrocyanide by suitable means, and distilling with dilute sulphuric acid into a solution of sodium or potassium hydroxide.

The methods Nos. 1, 2, and 4 are only accurate when used to estimate pure ferrocyanides ; No. 3 yields only comparative results, as no account is taken of the alkali metals which are always combined in varying proportion with the prussian blue, displacing some of the iron of the base.

Of the methods classed under No. 5. those involving the use of a solution of zinc or copper sulphate are in most general use. These methods have been subject to a number of modifications, and corrections, but are fairly accurate when all the precautions are carefully

observed, the chief difficulty is the correct observation of the end-point, which undoubtedly requires very considerable practice.

1. **Estimation of the total nitrogen by Kjeldahl's method.**

This method is carried out in the usual manner of a Kjeldahl determination, the nitrogen of the cyanogen group being very readily converted into ammonia.

Take 0.5 grm. of the dry ferrocyanide, or a quantity of dry material assumed to contain this amount of ferrocyanide, but free from other nitrogen compounds, and place in a long-necked flask of about 100 c.c. capacity, then add 10 to 15 c.c. of concentrated sulphuric acid, together with some crystals of potassium sulphate—no other additions are necessary—and heat on the sand bath or hot plate for about two hours. When this operation is complete, the flask is cooled and the contents washed out into a 500 c.c. distilling flask, with pure ammonia free distilled water, and the acid liquor made alkaline with a strong solution of sodium or potassium hydroxide. Care must, however, be taken to add the alkaline solution slowly, agitating the flask after each addition, to avoid a too violent action. The mixture in the flask is then made up to about 300 c.c. and distilled through a condenser into an absorption bottle containing 150 c.c. of N/10 sulphuric acid.

When the operation is complete and all the ammonia driven over into the standard acid, the latter is washed out and the excess of acid estimated by titration with a standard N/10 solution of alkali, using methyl orange as indicator. The amount of alkaline solution required to neutralize the excess of acid, deducted from 150 c.c., represents the amount of N/10 sulphuric acid neutralized by the ammonia. Each c.c. of N/10 sulphuric acid so neutralized is equivalent to 0.003532 grm. of ferrocyanogen, $'''Fe(CN)_6$, 0.004772 prussian blue, $Fe_4[Fe(CN)_6]_3$ or 0.006138 potassium ferrocyanide, $K_4Fe(CN)_6$.

This process is of course only accurate in the entire

absence of thiocyanates or any nitrogenous compounds other than ferrocyanides.

2. **Estimation of the ferrocyanogen iron.**

This method depends on the decomposition of ferrocyanides by ignition with strong sulphuric acid, and the estimation of the iron in the residue.

One gramme of the soluble ferrocyanide—or if the ferrocyanide exists as an insoluble compound such as prussian blue, a weighed quantity must first be decomposed by the minimum quantity of caustic soda or potash solution, filtered from the metallic base which must be thoroughly washed and the filtrate diluted to a definite volume : an aliquot part of this solution which should contain about 1 grm. of ferrocyanide is evaporated to dryness in a platinum dish—is treated with concentrated sulphuric acid and heated. The heat should be applied slowly at first, and the dish kept covered until the evolution of gas which at first takes place ceases; otherwise loss by spurting is liable to occur at this stage.

When this effervescence ceases, the mixture is more strongly heated, and the ferrocyanide completely decomposed, carbon monoxide, carbon dioxide and sulphur dioxide are evolved as gases, and the sulphates of iron and ammonium together with the alkali metal base of the ferrocyanide left in the dish with the excess of sulphuric acid. The latter may be driven off by heat under a hood. The residue in the dish is dissolved in distilled water to which a few drops of hydrochloric acid have been added to assist the solution of the ferric sulphate, and boiled. When the solution is complete it is washed out into a beaker and the iron estimated by any of the known methods.

To obtain the weight of ferrocyanide in the amount of material taken, the weight of ferric oxide found must be multiplied by 3.586 for prussian blue, $Fe_4[Fe(CN)_6]_3$, or $\times$ 4.613 for $K_4Fe(CN)_6$.

By boiling a solution of a ferrocyanide with an excess of ammonium persulphate, the ferrocyanide can be completely oxidized and decomposed, without the

necessity of first evaporating the solution to dryness, and the iron determined in the solution.

To a solution containing a ferrocyanide equivalent to about 1.0 grm. of potassium ferrocyanide, in not more than 70 c.c. of water a few drops of dilute (1 to 10) sulphuric are added and then 30 c.c. of a 10 per cent. solution of ammonium persulphate and the mixture heated on the water-bath. The first action of the persulphate is to convert the ferro into ferricyanide. This latter body is then decomposed with precipitation of a basic ferric sulphate which renders the liquid turbid, but gradually dissolves on further heating.

When the reaction is complete 10 c.c. of strong hydrochloric acid are added and the heating continued. The appearance of a blue colour at this stage indicates the presence of undecomposed iron cyanides, and more ammonium persulphate solution should be added to destroy it.

An excess of ammonia solution is then added and the precipitated ferric hydroxide filtered off and estimated by any convenient method.

The insoluble ferrocyanides can, of course, be estimated by this process if they are first decomposed by sodium hydroxide, filtered, washed and the filtrate treated as above.

This method, like the preceding, is only applicable to comparatively pure ferrocyanides. Crude ferrocyanides or ferrocyanide liquors, such as those obtained by the extraction of spent oxide or cyanogen mud with caustic alkalis, cannot be estimated by this method as they generally contain appreciable amounts of iron oxides in colloidal solution, which cannot be entirely eliminated by precipitating as the iron salt, and re-solution in caustic soda or potash solution.

3. **By Conversion into Prussian Blue and subsequent Ignition.**

Weigh out carefully about half a gramme of the ferrocyanide or measure out a portion of the solution known to contain about half a gramme of ferrocyanide, dilute to 100 c.c. and add to an excess of a boiling

dilute solution of an iron salt acidified with sulphuric or hydrochloric acid in a 500 c.c. beaker. When the precipitate has become clotty and begins to settle, the whole is filtered through a large sized pleated filter, thoroughly washed, dried and ignited in free contact with the air. The ash is then dissolved in hydrochloric acid and the iron estimated in the usual manner.

$$4Fe_4[Fe(CN)_6]_3 + 93O_2 = 14Fe_2O_3 + 36N_2 + 72CO_2.$$

To obtain the percentage of ferrocyanide multiply the ferric oxide obtained from the half-gramme by 1.537 × 200 for prussian blue, $Fe_4[Fe(CN)_6]_3$, or by 1.977 × 200 for potassium ferrocyanide, $K_4Fe(CN)_6$.

The ferrocyanide solution should be fairly pure and free from organic matter, otherwise organic iron compounds may be carried down with the prussian blue and thus increase the weight of ferric oxide.

With pure solutions, however, the method is inaccurate and is not to be recommended. The prussian blue obtained by the above method is not pure ferric ferrocyanide of the formula $Fe_4[Fe(CN)_6]_3$, but contains some alkali metal in combination displacing some of the basic iron, the amount and nature of which depend on the conditions of the precipitation and on the particular ferrocyanide used.

In the method described above for precipitating the blue, the least amount of alkali metal is retained, but even in this case the amount is sufficient to make an error of about 1½ per cent. when sodium ferrocyanide is used, and 2 per cent. with the potassium salt. The composition of the blue when prepared from sodium ferrocyanide in the manner described above agrees with the formula $Fe_{13}Na[Fe(CN)_6]_{10} = 3Fe_4[Fe(CN)_6]_3 : FeNaFe(CN)_6$, *i.e.*, three molecules of pure ferric ferrocyanide with one of ferric sodium ferrocyanide. When potassium ferrocyanide is used the error is greater because the composition of the precipitate formed under these conditions may be expressed by the formula, $Fe'''_9K[Fe(CN)_6]_7 = 2Fe_4[Fe(CN)_6]_3$:-

$FeKFe(CN)_6$, two molecules of pure ferric ferrocyanide to one of ferric potassium ferrocyanide.

Another source of error which tends to balance that just described, is that unless the boiling iron solution is made strongly acid a considerable proportion of ferric hydroxide is carried down with the colloidal blue precipitate.

The factor given above refers to anhydrous ferric ferrocyanide, but it must be remembered that prussian blue always contains variable amounts of combined water.

4. **By Oxidation to Ferricyanide.**

This method depends on the fact that by the addition of a suitable oxidizing agent, generally a solution of potassium permanganate, to a dilute and acidified solution of a ferrocyanide, the latter body is oxidized to a ferricyanide quantitatively, the end of the reaction being observed by the solution turning a yellowish-red due to a slight excess of permanganate.

To carry out the method 1.0 gramme of the ferrocyanide is dissolved in distilled water, or a measured volume of solution containing an equivalent quantity is taken and placed in a white porcelain dish of 1000 c.c. capacity and diluted to about 700 c.c. with distilled water. The mixture is then acidified with dilute sulphuric acid and standard N/10 permanganate solution added slowly with constant stirring, until the liquid which at first turns yellow owing to the formation of ferricyanide, changes to a reddish-yellow, indicating the complete conversion of the ferrocyanide according to the equation :

$$5K_4Fe''(CN)_6 + KMnO_4 + 4H_2SO_4 = 5K_3Fe'''(CN)_6 + 3K_2SO_4 + MnSO_4 + 4H_2O.$$

The standard solution of permanganate may be the ordinary N/10 solution or as is sometimes preferred a more dilute solution, say N/50, in which case not more than 0.2 grm. of the ferrocyanide is taken for the estimation.

The permanganate solution may be standardized

against pure recrystallized potassium ferrocyanide, or preferably the dry calcium potassium double salt. This compound is easily prepared pure and is quite anhydrous. 2½ grm. after drying at 100° C. are weighed out and decomposed by boiling with sodium or potassium carbonate, filtered, the precipitate washed and the filtrate diluted to 250 c.c.; 100 c.c. of this solution, equivalent to 1.0 grm., are taken for standardizing N/10 permanganate solution or 20 c.c. (0.2 grm.) for the N/50 solution.

Each cubic centimetre of N/10 permanganate solution required is equivalent to 0.03683 grm. $K_4Fe(CN)_6$ or 0.02119 grm. $Fe(CN)_6$ and 0.007366 and 0.004238 respectively for the N/50 solution.

This method has received a good deal of criticism and several modifications have been proposed. Thus E. Muller and O. Diefenthäler [1] state that accurate results are obtained by using solutions containing about 1 grm. of the ferrocyanide dissolved in 150 to 200 c.c. of water acidified with 20 c.c. of dilute sulphuric acid (1 to 4) and titrating the solution with N/20 permanganate solution until the colour changes to yellowish-red.

H. Bollenbach [2] suggests that the best method for carrying out this titration is to add the standard permanganate solution to the ferrocyanide solution strongly acidified with dilute sulphuric acid until the appearance of a distinct red-violet colour; a few drops of ferric sulphate solution are then added, and the excess permanganate titrated with standard N/20 potassium ferrocyanide. Each drop of the ferrocyanide solution produces a green precipitate which disappears on shaking as long as the permanganate is in excess.

The particular modification of this process that may be used is immaterial so long as the estimation is performed in exactly the same manner as the standard; but the method is only accurate in the absence of

[1] *Z. anorg. Chem.* (1910), **67**, 418–36.
[2] *Z. anal. Chem.*, **47**, 687–90.

compounds capable of reacting with the permanganate, such as thiocyanates, sulphites, thiosulphates, organic matter, etc., which would, of course, consume permanganate and yield too high a result.

Should other oxidizable matter be present, the ferrocyanide solution is first diluted to 250 c.c. made slightly acid with dilute sulphuric acid, and an excess of permanganate solution added which converts the ferrocyanide into ferricyanide, and oxidizes any other oxidizable compounds that may be present. The solution is then made alkaline with caustic soda solution in excess, followed by the addition of a solution of ferrous sulphate, and the mixture warmed: the precipitated ferrous hydroxide reduces the ferricyanide to ferrocyanide, but does not reduce the other oxidation products. The solution is filtered from the black ferrosoferric hydroxide and the latter thoroughly washed, the filtrate transferred to a porcelain dish, acidulated with dilute sulphuric acid, diluted, and titrated with the permanganate solution. In the second titration with permanganate only the ferrocyanide is oxidized.

In the presence of thiocyanates the results obtained by this method will be too high, for when these salts are oxidized by permanganate in the preliminary oxidation, sulphuric and hydrocyanic acids are formed, while in the subsequent treatment with caustic alkali and ferrous hydroxide the hydrocyanic acid is converted into ferrocyanide and thus increases the result. This difficulty may be readily overcome by first precipitating the ferrocyanides solution with ferric sulphate after acidification; the whole is then thrown on a pleated filter, and the blue precipitate thoroughly washed free from thiocyanates. The precipitated blue is then transferred to a beaker together with the filter-paper, and decomposed by a dilute solution of sodium or potassium hydroxide and the mixture again filtered and washed. The filtrate may then be acidified and diluted, and titrated with the standard permanganate solution in the above-described manner.

Instead of the precipitation method of purification described above, the measured volume of ferrocyanide solution may be first oxidized by an excess of permanganate in acid solution, and the ferricyanide reduced to ferrocyanide by the addition of freshly precipitated manganous or cobaltous hydroxides, after the solution has been made alkaline with caustic soda, or a salt of these metals mixed with an excess of alkaline hydroxide may be added. On warming the mixture the ferricyanide is immediately reduced: it is then filtered, the precipitate thoroughly washed and the ferrocyanide estimated in the filtrate.

This method, besides preventing the formation of ferrocyanide from any hydrocyanic acid that may have been liberated in the first oxidation, has the further advantage that a far less bulky precipitate is obtained, thus considerably facilitating the washing of the precipitate. But little additional manganous hydroxide need be added as the solution contains sufficient manganous salt to reduce the ferricyanide when the solution is rendered alkaline.

If the ferrocyanide solution contains uncrystallizable organic matter such as the liquor or mother liquor from a ferrocyanide works, and particularly that obtained by the extraction of spent oxide, this method should not be used, as it is practically impossible to obtain accurate results either by precipitation with a ferric salt, or by the preliminary oxidation with excess of permanganate.

As a ferricyanide does not liberate iodine from potassium iodide solutions in the presence of weak acetic acid and in the absence of zinc salts, a modification of the above process [1] is possible. An excess of permanganate solution is added, followed by a solution of potassium iodide, and the liberated iodine determined by N/10 sodium thiosulphate. A known quantity of about 0.5 grm. of the ferrocyanide is diluted to 600 c.c. and 10 to 15 c.c. of concentrated hydrochloric acid and 40 to 60 c.c. of a saturated solution

[1] W. Mekslenberg, *Z. anorg. Chem.*, **67**, 322–38.

of sodium acetate added, standard permanganate solution is then added in decided excess, followed by the addition of potassium iodide and the liberated iodine carefully titrated. As acetic acid is liable to contain reducing agents, this acid should not be substituted for the hydrochloric acid and sodium acetate.

5. **By Precipitation as a heavy metal Ferrocyanide.**

The titration of a solution of a ferrocyanide with a standard solution of a heavy metal salt, was first proposed by Bohlig, and afterwards worked out in detail by Knaublauch.[1]

An acidified solution of the ferrocyanide is precipitated by adding slowly from a burette a few drops at a time, a solution of known strength of a metallic salt until the whole of the ferrocyanide is precipitated. The precipitating value of each cubic centimetre of the metallic salt is obtained by a previous titration with a solution containing a known weight of a pure ferrocyanide.

The metallic salt usually used for this purpose is the sulphate of copper or zinc.

By Titration with Sulphate of Copper Solution.

The standard copper solution is prepared by dissolving 12½ grm. of pure recrystallized sulphate of copper in distilled water, adding 10 c.c. of 10 per cent. sulphuric acid, and then diluting the whole to 1000 c.c. This solution is standardized against a solution of a ferrocyanide of known strength, and adjusted until 1 c.c. of the copper solution will exactly precipitate ferrocyanide equivalent to 0.01 grm. of ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$.

The dry anhydrous double calcium potassium ferrocyanide should be used for standardizing the copper solution. This salt is easily prepared by adding a solution of calcium chloride to a moderately strong solution of pure potassium ferrocyanide. The double salt separates out in the cold, in small granular crystals which are anhydrous, the salt is filtered on a vacuum

[1] J. Gasbeleuckt (1889), **33**, 450.

filter, washed with distilled water and dried at 100° C., at which temperature it is perfectly stable : 1.153 grm. of this salt is equivalent to 1 grm. of ferric ferrocyanide. The standard solution is prepared by taking this weight of the double salt and converting it into the potassium compound by boiling with a solution of potassium carbonate, filtering and thoroughly washing the precipitated carbonate of calcium and diluting the filtrate to 100 c.c.

Measure out 20 c.c. of the standard ferrocyanide solution into a precipitating beaker of about 150 c.c. capacity, acidify with 25 c.c. N5/– sulphuric acid and 20 c.c. of a saturated solution of potassium chloride : this latter addition is necessary, as will be explained later. The copper solution is now run in slowly from a burette, the liquor being agitated gently the while, until the whole of the ferrocyanide is precipitated. The end-point is observed by taking a strip of filter-paper about 1½ in. long and ¾ in. wide, and dipping it into the liquid so that about one-third is submerged. The strip is removed and the clear liquor which sucks up away from the brown precipitate of cupric ferrocyanide is touched with a glass rod that has been dipped in a dilute solution of ferric chloride. Any ferrocyanide still in solution will produce a blue coloration at the junction of the two liquids, care of course being taken that the iron salt does not touch the brown precipitate of copper ferrocyanide. This formation of a blue coloration indicates that ferrocyanide is still in solution, and that more copper solution must be added. As the blue colour becomes less and less, smaller quantities of the copper solution should be added after each test. This test, as with any other volumetric process, should always be performed in duplicate ; in the first the standard solution is added ½ c.c. at a time, and the result obtained between limits ; in the second the standard solution may be run in to the lower limit, the point at which the blue was last seen in the previous titration, and then added very gradually until the exact end-point

is obtained, and no blue colour appears on the test-paper after the lapse of one minute. This test should be repeated with a second test-paper.

Ferrocyanide estimations must be carried out in an exactly similar manner to that of the standardization.

This method yields excellent results if carried out exactly in the manner described above, but undoubtedly requires some considerable practice. The points to be particularly observed in order to obtain accurate results are :

1. The total volume of liquid titrated should be about the same in each operation, and the same as that used for the standard.

2. As near as possible, the same amount of ferrocyanide should be present in each test.

3. It is essential that potassium salts should be in excess in the liquid, such as the chloride or sulphate, and also if caustic alkali has been used to decompose an insoluble ferrocyanide, this alkali must be caustic potash, and not caustic soda.

4. When standardizing the copper solution the warning given in No. 3 must be observed, potassium and not sodium ferrocyanide must be used, and an excess of potassium chloride or sulphate added before titration.

Failure to observe the warnings given in 3 and 4 has been the cause of much discrepancy in the results obtained by different workers when using this method. The reason of this variation is that the amount of copper required to precipitate a known weight of potassium ferrocyanide, does not correspond with the theoretical amount required for the formation of pure cupric ferrocyanide, $Cu_2Fe(CN)_6$, but is considerably less. The composition of the precipitate in presence of excess of potassium salts corresponds with the formula, $Cu_6K_8[Fe(CN)_6]_5$, and contains only three-fifths of the theoretical copper. If the potassium salts are not in excess, copper ferrocyanide containing less potassium, and therefore more copper, are pre-

cipitated, such as the compounds $Cu_4K_4[Fe(CN)_6]_3$ and $Cu_3K_2[Fe(CN)_6]_2$.

With sodium ferrocyanide in the presence of excess of sodium salts, a large proportion of sodium is carried down combined with the copper ferrocyanide precipitate, although the amount is considerably less than that of potassium combined with the precipitate produced from potassium ferrocyanide under similar circumstances.

The addition of an excess of potassium sulphate or chloride to a soluble ferrocyanide such as the sodium or calcium salt, will on titration with the copper solution produce a precipitate containing potassium, but wholly free from sodium or calcium, and the composition of the precipitate is the same as that formed from pure potassium ferrocyanide, containing excess of potassium salts. Thus these ferrocyanides can be accurately estimated by this method if an excess of potassium salts is added, but the solution should be free from ammonium salts.

Instead of strips of filter-paper, the end-point is sometimes determined by filtering a portion of the liquid through a small filter-paper and testing the filtrate with a few drops of the copper solution. The formation of a brown coloration or precipitate indicates an incomplete reaction, the filtrate and liquor on the filter are then poured back into the titration beaker, and some more copper solution added, and a further portion again filtered and tested in a similar manner. This method offers no advantage over that previously described, and is far more tedious, but should it be adopted care must be taken to see that the filtrate is quite clear before testing with the copper salt, for frequently a small portion of very finely divided copper ferrocyanide passes through the filter-paper, which would greatly interfere with the test. It is also essential that the standardization of the copper solution with potassium ferrocyanide should be performed in a similar manner and under the same conditions.

Drop reaction-paper such as that of Schuler and Schule is frequently substituted for the strips of filter-paper with excellent results, but the author, from the experience of many thousands of tests by this method, prefers to use the filter-paper strips, and here again it is necessary that the same brand of filter-paper is used for the estimation as for the standardization.

In the analysis of crude ferrocyanide liquors or the extract of spent oxide of iron, the solution must first receive a preliminary purification. This is usually accomplished by acidifying a definite volume of the solution containing the alkaline extract from 5 grm. of the spent oxide, with dilute sulphuric acid followed by an excess of ferric chloride. The mixture is left for a short time to allow the prussian blue to clot and begin to settle. It is then thrown on to a large pleated filter, allowed to drain and thoroughly washed with water to remove all thiocyanates, and other soluble impurities.

The washed precipitate, together with the filter-paper, is then returned to the beaker in which it was originally precipitated, and digested with 50 c.c. of a solution of 5 per cent. potassium hydroxide, stirred with a glass rod until all the blue is decomposed. The mixture is then transferred to a flask and diluted to 250 c.c. without filtration, and no allowance is made for the space occupied by the paper. The liquid is then well shaken and filtered.

Fifty cubic centimetres of the filtrate (= 1 grm. spent oxide) are taken, acidified with dilute sulphuric acid, 20 c.c. of potassium chloride solution added, and titrated with the standard copper as described. The liquor, before titrating with the copper, should be tested for sulphides, and if found to be present it should be warmed with an excess of lead carbonate, filtered and washed and the solution titrated. In the presence of excess of organic matter the results obtained by this method are liable to be too low. This question is discussed fully under analysis of spent oxides.

Titration with Zinc Sulphate Solution. The principle of this method is the same as the copper method described above, but it is usual to work with stronger solutions, and about 1 grm. of ferrocyanide is taken for each determination.

Dr. F. W. Skirrow [1] has investigated this process, and recommends a solution of 46.5 grm. of crystallized zinc sulphate per litre, and states that it is immaterial whether the alkaline ferrocyanide is pure or contains dissolved in its solution soluble salts of the same alkali metal, but that in the latter case a longer time is required to obtain a definite end-point.

This process which has been extensively used by the author, has been found to give excellent results, and the observations of Skirrow mostly confirmed, and that the presence or absence of excess of sodium, potassium, or ammonium salts with solutions of the corresponding ferrocyanide have but little effect on the result of the titration, if sufficient time is allowed before testing for the end-point; but it was found advisable to add them, and the results so obtained were more concordant than in the absence of these salts. It was also found that the amount of zinc required to precipitate each equivalent of ferrocyanide differed a little for each base, but that if the solution were standardized by potassium ferrocyanide, accurate and comparative results could be obtained in the precipitation of ferrocyanides of other bases if an excess of potassium sulphate or chloride were added before titration.

The precipitate produced is not pure zinc ferrocyanide, $Zn_2Fe(CN)_6$, but contains 75 per cent. of the zinc theoretically required for the above formula, so that the white precipitate is more or less pure double zinc potassium ferrocyanide corresponding to the formula $Zn_3K_2[Fe(CN)_6]_2$.

In this method as in the preceding, the same possible sources of error must be guarded against, the same volume of liquor should be taken for each test, and

[1] *J.S.C.I.*, **29**, 319–23.

similar proportions of acid and excess of potassium salts should be present, if the zinc solution has been standardized on potassium ferrocyanide. The end point may also be detected by any of the methods described for the copper titration, but it will be found that either the strips of filter-paper or the drop reaction test will be best.

Ferric chloride solution, and the salts of other heavy metals have been proposed in place of either copper or zinc for the estimation of ferrocyanides, but they are not so convenient and offer no advantage over those already described.

Estimation by Zinc Carbonate.—When an excess of zinc carbonate is digested in a neutral solution of a ferrocyanide and carbon dioxide passed through the mixture a reaction takes place, thus with potassium ferrocyanide :

$$4K_4Fe(CN)_6 + 4ZnCO_2 = Zn_4K_4[Fe(CN)_6]_3 + 4K_2CO_3.$$

the potassium carbonate liberated may be titrated with standard acid, and thus a measure of the ferrocyanide obtained.[1]

The above reaction with potassium ferrocyanide takes place in both hot or cold solution, but with sodium ferrocyanide the solution must be heated.

Estimation with Cupric Sulphate after oxidation to Ferricyanide. This method, which has been proposed by F. Hurter,[2] is carried out in the following manner.

A definite volume of the solution is boiled with sufficient bleaching-powder solution to oxidize the ferrocyanide to ferricyanide and completely to oxidize all other oxidizable compounds that may be present. The liquid is then just acidified, and the chlorine in excess removed by agitation and warming.

The solution thus prepared is then titrated with a N/10 cupric sulphate solution, when the ferricyanide is precipitated as the yellowish-green cupric ferricyanide. The end-point may be determined by placing

[1] R. Zaloziecki, *Z. anal. Chem.*, **30**, 484.

[2] *Chem. News*, **39**, 25.

a drop of the thoroughly agitated liquid on a clean porcelain tile, and adding a drop of a dilute solution of the double ferrous ammonium sulphate ; the formation of a blue colour indicates the presence of ferricyanide still in solution, and more copper solution must be added until on testing the liquid, no blue coloration can be detected. At this point the ferrous salt will reduce the green cupric ferricyanide to the chocolate-brown colour of the cupric ferrocyanide. As the precipitate is almost pure cupric ferricyanide containing only a small proportion of potassium (less than 0.1 per cent.), 1 c.c. of the standard solution is equivalent to 0.007067$Fe(CN)_6$.

This method does not seem to offer any great advantage over the direct titration of the ferrocyanide with copper salts. It is claimed that the ferrocyanides may be estimated in the presence of cyanate, thiocyanate, cyanide, sulphide and thiosulphate, etc., but the ferrocyanide can be readily separated from these salts by simple precipitation as the blue iron salt.

Estimation as Hydrocyanic Acid. When a solution of a ferrocyanide of the alkali or alkaline earth metals is distilled with a dilute mineral acid, hydrocyanic acid is evolved, but the action does not proceed to completion, for the ferrous salt formed by the decomposition of one molecule of the ferrocyanide, combines with another molecule of the ferrocyanide to form an insoluble ferrous ferrocyanide which resists the action of dilute mineral acids. Thus with potassium ferrocyanide only 50 per cent. of the total cyanogen is obtained as hydrocyanic acid. the course of the reaction may be expressed as follows :

$$2K_4Fe(CN)_6 + 3H_2SO_4 = 6HCN + Fe''K_2Fe(CN)_6 + 3K_2SO_4.$$

When sodium, ammonium or magnesium ferrocyanides are substituted for the potassium salt, the reaction proceeds in a similar manner.

The ferrocyanides of the alkaline earth metals, including the lithium and hydrogen salt, when treated

in this way yield two-thirds of their total cyanogen as hydrocyanic acid, due to the fact that apparently no double ferrous ferrocyanides of these bases exist. The action therefore takes place according to the equation:

$$3Ca_2Fe(CN)_6 + 6H_2SO_4 = 12HCN + Fe''_2Fe(CN)_6 + 6CaSO_4,$$

and pure ferrous ferrocyanide is precipitated. This insoluble salt decomposes very slowly when boiled with dilute acids; by increasing the strength of the acid decomposition proceeds at a somewhat greater rate, but with moderately strong mineral acids some of the hydrocyanic acid is destroyed with formation of ammonium formate and thus lost.

Attempts have been made to break up the ferrocyanogen grouping, and so prevent the formation of these insoluble ferrous ferrocyanide compounds, in order to obtain the whole of the cyanogen in the form of hydrocyanic acid.

If a soluble ferrocyanide is boiled with mercuric chloride or oxide, the ferrocyanide is decomposed with formation of mercuric cyanide, which on subsequent distillation with dilute mineral acids, can be made to yield the whole of the cyanogen as hydrocyanic acid without the formation of insoluble cyanogen compounds.

The estimation of ferrocyanides by first boiling with mercury salts was first proposed by Rose and Finkener,[1] and afterwards developed in detail by W. Feld.[2]

To a portion of the material or an aliquot part of the solution known to contain about 0.5 grm. of ferrocyanide, diluted to 150 c.c. with distilled water, 10 c.c. of N/– sodium hydroxide solution are added, and the mixture boiled to convert any possible insoluble ferrocyanide that may be present into the soluble sodium salt. After boiling for ten minutes or so, 15 c.c. of a 30 per cent. solution of magnesium chloride are then added gradually with continued agitation to obtain a precipitate of magnesium hydroxide in a fine

[1] *Z. anal. Chem.* (1862), 1, 299.

[2] J. Gasbeleucht (1903), **46**, 565; *J.S.C.I.* (1903), 1068.

state of division and to avoid the formation of clots; the mixture is again boiled, and then 100 c.c. of N/10 mercuric chloride are added and the whole boiled for about a quarter of an hour. By these means the whole of the ferrocyanide is decomposed and converted into mercuric cyanide.

The mixture is then transferred to a distilling flask fitted to a condenser connected to an absorption bottle containing pure dilute sodium or potassium hydroxide solution, 25 c.c. of 5N/– sulphuric acid are then added and the liquid distilled until the mercuric cyanide is decomposed and all the hydrocyanic acid driven over and absorbed in the alkaline solution. The cyanide solution is removed from the absorption bottle into a titration beaker, and the condenser and bottle thoroughly washed out with distilled water, a few drops of a 10 per cent. solution of potassium iodide are added, and the liquid titrated with standard N/10 solution of nitrate of silver, until the first appearance of a faint but permanent turbidity.

In this process great care is required in the preliminary mixing of the solutions, the magnesium chloride must be added slowly and carefully to the alkaline solution so that a uniform precipitate is obtained throughout the mass, otherwise clots are liable to form which may cause a portion of the ferrocyanide to escape decomposition in the subsequent boiling with the mercuric chloride, and thus an error of 1 or 2 per cent. may occur.

The process has been subject to some criticism by F. W. Skirrow,[1] by whom it is stated that some considerable losses occur, particularly in the preliminary boiling operations; on the other hand H. G. Coleman[2] states that in his hands the process has yielded theoretical results.

Decomposition of the Ferrocyanogen by means of Cuprous Chloride. The principle of this method[3] rests on the fact that when cuprous chloride is added

[1] *J.S.C.I.* (1910), 319. [2] *Analyst* (1910), **35**, 295.
[3] H. E. Williams, *J.S.C.I.*, **315** (1912).

to an acid solution of a ferrocyanide, complex cuprous cyanides are formed, which are easily decomposed by boiling with a dilute mineral acid, with evolution of hydrocyanic acid, and regeneration of the cuprous chloride which is thus available for the decomposition of a further quantity of ferrocyanide. As these two reactions can proceed simultaneously, the complete decomposition of the ferrocyanide may be accomplished in one operation and with a relatively small quantity of cuprous chloride.

The best method of carrying out the process is to take 0.5 grm. of the ferrocyanide dissolved in water, or a volume of solution containing an equivalent quantity and place in a distilling flask of about 350 to 400 c.c. capacity, and dilute to about 150 c.c. Weigh out 0.1 to 0.05 grm. of cuprous chloride, wash in a small beaker with a little dilute sulphuric acid to remove any basic cupric chloride that is generally present, and dissolve in a few drops of hydrochloric acid, or in a saturated solution of sodium or potassium chloride, and add to the ferrocyanide solution in the distilling flask with gentle agitation. A white precipitate is produced of a double cuprous ferrocyanide; 50 c.c. of 4N/- sulphuric acid are then added, the flask connected to a condenser to which are attached two absorption flasks containing a dilute solution of sodium or potassium hydroxide, and gently distilled. After a few minutes boiling the white precipitate changes to light blue, due to the precipitation of the double ferrous ferrocyanide: this precipitate is then slowly decomposed and ultimately the solution becomes quite clear, the whole of the ferrocyanide being decomposed and the cyanogen driven off as hydrocyanic acid, leaving a solution containing ferrous sulphate, and a bisulphate of the alkali metal used, together with the excess of sulphuric acid, and the regenerated cuprous chloride.

The alkaline solution in the absorption flasks is carefully washed out into a titrating beaker, a few drops of a 10 per cent. solution of potassium iodide

added, and the liquor titrated with N/10 silver nitrate solution while being agitated, until the first appearance of a permanent opalescence, which does not disappear on further agitation.

One cubic centimetre of N/10 silver nitrate solution is equivalent to 0.0070633 grm. ferrocyanogen$'''[Fe(CN)_6]$; 0.009545 grm. ferric ferrocyanide, $Fe'''_4[Fe(CN)_6]_3$; and 0.012277 grm. potassium ferrocyanide, $K_4Fe(CN)_6$.

This method has the advantage over the preceding in that it requires no preliminary boiling or other treatment, and it can be applied to any ferrocyanide whether soluble or insoluble. The double sparingly soluble ferrocyanides of the alkali and alkaline earth metals or the insoluble ferrocyanides of the heavy metals such as those of iron, copper, zinc, cadmium or nickel, etc., being readily decomposed. If the insoluble ferrocyanide is in the dry state it must, of course, be first ground to powder before adding to the distilling flask, and in the case of the ferric ferrocyanides, a little more cuprous chloride than the amount mentioned above should be added. But if the insoluble heavy metal ferrocyanide is hard and gritty, the decomposition will be very slow, and it will be found more convenient to decompose it first with caustic soda or potash.

All that is necessary to determine the cyanogen contents of the insoluble ferrocyanides is to add 0.5 grm. of the finely powdered or precipitated ferrocyanide to the distilling flask with 100 to 150 c.c. of water and the requisite quantity of dilute sulphuric acid and cuprous chloride, and to distil into the caustic alkali solution.

With this method any alteration in the order in which the materials are added will make practically no difference. The solution of the cuprous salt in a solution of a soluble chloride considerably increases the rate of decomposition, not only because it introduces the cuprous salt in a more finely divided state, but also because it increases the proportion of chlorine ions in the solution and thus considerably increases the

rate of regeneration of the cuprous chloride from the cuprous cyanide in the acid solution.

The use of a larger proportion of cuprous chloride than the amount given offers no advantage, and the minimum quantity of chloride solution should be used to dissolve it.

Ferrocyanides intermixed with other bodies, such as prussian blue in dyed or weighted silk, or in spent oxide of iron, can also be estimated direct by this method. A weighed quantity of the material is added to the distilling flask with the other ingredients and distilled, when the whole of the ferrocyanogen in the material will be decomposed and the cyanogen evolved as hydrocyanic acid.[1]

Estimation of Ferrocyanides as Silver Cyanide. This process[2] depends upon the action of an ammoniacal solution of silver nitrate on ferrocyanide at 100° C., which it completely decomposes into the hydroxides of iron and the base of the ferrocyanide and silver cyanide. A weighed portion of the ferrocyanide is heated to 100° C. in a sealed tube with an excess of a solution of ammoniacal silver nitrate for four to five hours. The tube is then cooled and unsealed, and the contents washed out into a dish, warmed to dissolve any double silver cyanide which may have separated, filtered from the metallic hydroxides and washed with ammonia.

The silver cyanide is precipitated by acidifying with dilute nitric acid.

ESTIMATION OF FERROCYANIDES IN SPENT OXIDE OF IRON AND CYANOGEN MUD

Estimation in Spent Oxide of Iron. Spent oxide of iron resulting from the purification of coal-gas, invariably contains some complex iron ammonia ferrocyanide compounds in amounts varying from a trace to 6 or 7 per cent. calculated as prussian blue, but

[1] Williams and Dreaper, *J. S. Dy. and Col.* (November 1912).

[2] W. Weith, *Z. Anal. Chem.*, 9, 379.

much higher percentages are frequently met with on the continent, particularly in Germany.

At one time—and that but a few years ago—the value of a spent oxide depended principally on its ferrocyanogen contents, though in recent years, chiefly owing to lower prices ruling for cyanide and ferrocyanide, and the expense and difficulty of recovering the ferrocyanides, spent oxide has but little interest for the makers of ferrocyanide or cyanide.

The method for estimating ferrocyanide in spent oxide in most general use, and for the most part adopted by the trade, is a modification of Knaublauch's copper method.

The spent oxide is dried in an air-oven, at a temperature not exceeding 60° C., for above this temperature a trace of the ferrocyanide may be decomposed and some of the cyanogen lost as ammonium cyanide; 25 grm. of the so dried material are weighed out, after grinding and sifting through a 60 mesh sieve, and digested in 100 c.c. of a 10 per cent. solution of potassium hydroxide, and left in the cold with frequent stirring for from eighteen to twenty hours. The whole mixture both soluble and insoluble matter together, is then poured into a graduated flask and diluted to 260 c.c., 10 c.c. being allowed for the bulk of the insoluble portion of the spent oxide. After thorough agitation, the solution is filtered through a large paper and 100 c.c. of the clear filtrate measured into a glass beaker of 200 to 250 c.c. capacity, acidified with dilute sulphuric acid, and ferric sulphate or chloride added in large excess. The blue mixture, after being well stirred with a glass rod, is allowed to stand ten to fifteen minutes to allow the blue to clot together and begin to settle. It is then thrown on a large pleated filter of about 18 cm. diameter, which has been previously wetted with distilled water, and the clear liquor allowed to drain through, and the blue precipitate thoroughly washed with boiling distilled water. In this manner the ferrocyanide is separated from the thiocyanate and other soluble impurities. When

thoroughly washed, the blue together with the filter-paper is removed from the funnel and placed in the beaker in which the blue was precipitated, 100 c.c. of a 5 per cent. solution of potassium hydroxide added, and the contents carefully stirred until all the blue is completely decomposed. The whole is then diluted to 250 c.c. without filtration and making no allowance for the volume of the paper. Heat must not be applied to decompose the blue, and the mixture should be diluted directly all the blue is decomposed, and not allowed to stand for any length of time in the strongly alkaline solution, or the free sulphur which is almost always precipitated along with the blue will pass into solution as a sulphide and thiosulphate of potassium. After dilution the flask is well shaken and the contents filtered through a large dry filter into a dry beaker.

For the estimation of the ferrocyanide 50 c.c. of the filtered liquor obtained as above, which will contain the ferrocyanide of 2 grm. of spent oxide, and which must be free from alkaline sulphide or polysulphide, are acidified with dilute sulphuric acid and titrated with standard sulphate of copper solution in the manner previously described.

If sulphides are found to exist in the alkaline ferrocyanide solution, they must be decomposed or removed before titration with the copper solution, or results much in excess of the truth will be obtained. Their removal is usually accomplished by agitating the liquid with pure lead carbonate, the solution filtered and the insoluble lead compounds thoroughly washed. The filtrate, after acidification, can then be titrated with the copper solution.

If the copper solution used is standardized so that 1 c.c. will exactly precipitate 0.01 grm. of ferric ferrocyanide, $Fe'''_4[Fe(CN)_6]_3$, then as the ferrocyanide corresponding to 2 grm. of spent oxide were taken, the number of cubic centimetres of copper solution used divided by two will express the percentage of ferrocyanide calculated as $Fe'''_4[Fe(CN)_6]_3$, in the spent oxide on the dry basis.

The results obtained by this method are generally a little too low, the reasons of this error are twofold: first, that as the blue is precipitated in the presence of some ammonium salts, derived from the spent oxide, it contains combined ammonium, which passes into solution when the blue is decomposed with an alkali, and occurs in the final solution as an ammonium salt. Now a little less copper is required to precipitate a ferrocyanide in the presence of ammonium salts than with potassium salts, thus the results obtained may be too low from this cause, and it is advisable to boil the purified alkaline ferrocyanide solution to drive off all ammonia and cool the liquid before titrating with the copper solution. For the same reason, a solution of ferric ammonium alum should not be used in place of ferric chloride or sulphate in the preliminary precipitation of the blue. Second, that when the crude alkaline solution obtained from the spent oxide is acidified and precipitated with an iron salt some organic matter soluble in the alkaline liquid but insoluble in dilute acid solutions is precipitated with the blue, and again passes into solution when the blue is subsequently decomposed by the caustic solution. This organic matter would, however, not interfere with the determination of the ferrocyanide alone, but by its agency some ferric oxide is carried into colloidal solution in the alkaline liquid. When this liquid is neutralized with dilute acid, the organic matter is precipitated together with the ferric oxide, which in the acid solution combines with an equivalent quantity of ferrocyanide, which thus escapes estimation with the copper solution and renders the result slightly too low.[1]

Standard sulphate of zinc may be substituted for the copper solution in the titration of the purified ferrocyanide, but with no material advantage; but caustic soda must not on any account be used in place of caustic potash, if the heavy metal solution has been standardized on potassium ferrocyanide.

[1] H. E. Williams, *J.S.C.I.*, **31**, 315.

Estimation of the iron of the ferrocyanide by evaporating the purified ferrocyanide liquor to dryness with excess of strong sulphuric acid, and estimating the iron in the residue will generally yield results far in excess of the truth, owing to the fact previously mentioned, *i.e.*, that some ferric oxide exists in colloidal solution due to the organic matter dissolved by the alkaline liquid. Equally inaccurate, for the same and other reasons is the method of estimating the ferric oxide in the precipitated, dried and ignited prussian blue, errors to the extent of 10 per cent. in excess of the true figure may occur by this means.

Up to a few years ago considerable discrepancies occurred in the analysis of the ferrocyanide contents of a spent oxide by different operators, owing to the want of thorough understanding of the process used, and to the use of methods entirely unsuitable. Errors of 10 per cent. in excess of the truth occurred by estimating the ferrocyanide on a sodium instead of a potassium basis, with a metallic solution standardized with potassium ferrocyanide, and errors of far greater extent occurred by using methods based on the estimation of the iron of the ferrocyanogen, or the ferric oxide left after ignition of the blue precipitate. The latter method is not only liable to the errors peculiar to spent oxide already mentioned, but to the fact, as little realized then as now, that in the presence of alkali metal salts or ammonium, the blue precipitate obtained is never ferric ferrocyanide, $Fe'''_4[Fe(CN)_6]_3$, but contains the alkali metal in combination displacing some of the basic iron, the amount of which depends entirely on the method of precipitation and the nature and amount of alkali metal salts also present in solution.

By first extracting the sulphur, by repeatedly washing the dry spent oxide with carbon disulphide, and then boiling the dried residue with dilute caustic potash solution, a dark coloured alkaline extract is obtained that will frequently yield a slightly higher percentage of ferrocyanide calculated on the original

spent oxide basis, than the figure obtained without extracting the sulphur—although when the latter method is used no ferrocyanide is left undissolved in the insoluble residue. The reason of this discrepancy is probably due to the fact that spent oxides appear to contain cyanogen compounds other than ferrocyanides or thiocyanates, which when treated with caustic alkalis in presence of sulphur appear as thiocyanates, but when boiled with the alkali after removal of the sulphur a portion of these compounds is converted into ferrocyanides. This is borne out by the fact that the alkaline extract obtained from the untreated spent oxide, contains a larger proportion of thiocyanates than the extract obtained from the sulphur-free material.

That certain spent oxides contain cyanogen-bearing compounds other than ferrocyanide or thiocyanate is clearly shown by the following example. A spent oxide containing a fairly high proportion of blue, and carefully washed with carbon disulphide to remove all sulphur, and dried, was examined and an analysis made of its nitrogen contents as follows : [1]

	Percentages in original dry spent.
Total nitrogen	4.595
Nitrogen in ammonia and pyridine . . .	1.238
Nitrogen in ferrocyanide and carbonylferrocyanide	2.400
Nitrogen in thiocyanates	0.210
	——3.848
Nitrogen unaccounted for . . .	.747

That this 0.747 is probably in the form of a cyanogen compound is shown by the following experiment. A weighed quantity of the original spent oxide, before removal of the sulphur, was boiled for some time with an excess of a moderately strong solution of caustic potash, and the nitrogen in its various forms again estimated, the ammonia was determined by absorbing the vapour given off the boiling caustic solution, in standard N/10 sulphuric acid.

[1] *J.S.C.I.*, 315, 31.

	Percentage in original dry spent oxide.	
Total nitrogen		4.595
Nitrogen combined as ammonia and pyridine	1.238	
Nitrogen combined as ferrocyanides and carbonyl-ferrocyanides	2.168	
Nitrogen combined as thiocyanates	1.158	
		4.564
Nitrogen unaccounted for		.031

Again a weighed quantity of the dried unextracted spent oxide was heated for some time with an excess of alkali under a pressure of 30 lb. per sq. in. and the nitrogen contents again examined :

	Percentage in original dry spent oxide.	
Total nitrogen		4.595
Nitrogen combined as ammonia and pyridine	1.238	
Nitrogen combined as ferrocyanides and carbonyl-ferrocyanide	—	
Nitrogen combined as thiocyanates	3.325	
		4.563
Nitrogen unaccounted for		.032

This formation of thiocyanates when the spent oxide is treated with an excess of caustic alkali and heated, does not occur with all spent oxides, but was generally found associated with those of high blue contents.

In order to lessen the time required by Knaublauch's method of estimating the ferrocyanide contents of spent oxide, J. W. Popplewell [1] proposed to boil a weighed quantity of the ground spent oxide with a weak caustic soda solution, instead of letting it stand in the cold alkaline solution for some hours, the extract to be diluted to a definite volume, an aliquot portion of the filtered solution acidified with dilute sulphuric acid, the ferrocyanide precipitated with an excess of ferric chloride solution, and the blue precipi-

[1] *J.S.C.I.*, **20**, 225.

tate filtered, washed, and estimated in the manner described.

The method is to be performed as follows :

Five grammes of the ground spent oxide are boiled in a beaker with 50 c.c. of a 5 per cent. solution of caustic soda for five minutes, and filtered and washed ; the filtrate is boiled, ferric chloride added in excess, and then acidified with dilute sulphuric or hydrochloric acid. Prussian blue is precipitated together with a considerable quantity of sulphur, the blue precipitate is thrown on a large pleated filter and thoroughly washed. It is then decomposed with a solution of caustic soda in the usual manner, filtered, and the precipitate washed, and the filtrate diluted to a definite volume ; a portion of the solution is then acidified and titrated with the copper solution in the manner described.

The above modification of Knaublauch's method is certainly more rapid than the original, but can scarcely be so accurate, for in the preliminary boiling in caustic soda solution, much sulphur will be dissolved as polysulphide, which will destroy some of the ferrocyanide with formation of thiocyanate ; indeed the digestion of the spent oxide in the cold in Knaublauch's method, was with the object of avoiding this loss. Again in Popplewell's modification caustic soda solution is used as the extracting alkali, but it must be remembered that if sodium ferrocyanide is titrated with sulphate of copper solution a result considerably in excess of the truth will be obtained if the copper solution were originally standardized with potassium ferrocyanide. This error could be avoided if potassium chloride solution were added before titration. The two sources of error mentioned above would tend to compensate one another. It would be necessary to treat the final liquor with lead carbonate to remove sulphide, which is bound to be present owing to the large amount of sulphur precipitated with the blue. Standard zinc solution could be here substituted with advantage for the copper salt, as the former would not

be influenced by the presence of thiocyanates or sulphides in solution.

A simple and at the same time a most accurate method of estimating the ferrocyanides in a spent oxide is by a modification of the cuprous chloride process.[1]

The spent oxide, after drying at 60° C., is finely ground and 10 grm. carefully weighed out, and the sulphur completely extracted by bisulphide of carbon, the residue is dried and boiled with a convenient quantity of a 5 per cent. solution of potassium or sodium hydroxide—the alkali used in this method is immaterial. After boiling for ten minutes the mixture is diluted to 253 c.c., the extra 3 c.c. being allowed for the volume of the insoluble matter. The liquid is then thoroughly mixed and filtered; 100 c.c. of the clear filtrate are poured into a distilling flask of 250 c.c. capacity, 0.1 to 0.05 grm. of cuprous chloride dissolved in a few drops of hydrochloric acid is then added, the solution is just neutralized with dilute sulphuric acid, an excess of 50 c.c. 5N/– sulphuric acid added and the mixture distilled through a condenser into a dilute caustic soda or potash solution. When the distillation is complete, the cyanide solution is washed out into a beaker, a few drops of potassium iodide solution added, and titrated with N/10 silver nitrate solution: 1 c.c. N/10$AgNO_3$ is equivalent to 0.009545 $Fe_4[Fe(CN)_6]_3$.

The advantages of this method are first that by removing the sulphur the total amount of ferrocyanides existing in the spent oxide is obtained in the alkaline solution, and secondly, an accurate estimation is obtained of the ferrocyanide in solution, unhampered by the presence of colloidal iron, as would be the case if the liquid were titrated with a heavy metal salt solution.

The ferrocyanide of a spent oxide can be directly estimated without previously removing the sulphur or extracting the ferrocyanide, by taking 2 grm. of the finely

[1] *J.S.C.I.*, 315, 31.

ground spent oxide and placing them in a distilling flask of about 200 c.c. capacity, together with 50 c.c. of distilled water, 50 c.c. of 5N/– sulphuric acid and 0.2 to 0.25 grm. of cuprous chloride dissolved in the smallest quantity of hydrochloric acid, and gently distilled into caustic soda solution. The presence of sulphur does not interfere with the determination, but the decomposition is slow.

By first removing the sulphur, and then distilling a weighed quantity with dilute acid and cuprous chloride, the reaction proceeds much more rapidly, and accurate results are obtained, agreeing exactly with the figure obtained by distilling the alkaline extract.

The ferrocyanide in a spent oxide can also be determined by the method proposed by Drehschmidt,[1] and modified by Burschell, by which the ferrocyanide is converted into mercuric cyanide by boiling with mercuric oxide, and estimating the hydrocyanic acid by distilling the mercuric cyanide with an acid.

The ferrocyanides are first extracted by treating a weighed quantity of the spent oxide with a solution of caustic soda or potash, and the alkaline solution acidified and precipitated as prussian blue by the addition of ferric chloride. The blue, after filtration and thorough washing, is converted into mercuric cyanide by boiling with mercuric oxide, and the filtered solution distilled with an acid, the evolved hydrocyanic acid being condensed in an excess of standard silver nitrate solution. The excess of silver left in solution is determined by titration with standard ammonium thiocyanate.

The alkaline ferrocyanide solution may also be converted into mercuric cyanide by boiling with mercuric chloride and distilling with an acid according to Feld's method described under ferrocyanide analysis.

Yet another method has been proposed for the estimation of ferrocyanides in spent oxides by A. O.

[1] *Muspratt's Chemie*, vol. v., p. 505, 4th German ed.

Nauss.[1] The ferrocyanide is extracted from a known weight of the spent oxide in the usual manner, diluted to a definite volume and an aliquot part measured into a beaker acidified with dilute sulphuric acid, and the ferrocyanide precipitated with an iron salt. The blue precipitate is then filtered and thoroughly washed, and decomposed with an excess of standard alkali. When the decomposition is complete the excess of alkali is titrated with N/10 acid. The end-point is shown by the first appearance of a pale green colour.

This process would be fairly accurate if the blue precipitate obtained were pure ferric ferrocyanide. Unfortunately it is impossible to obtain this compound by precipitating the blue in the presence of salts of the alkali metal.

When prepared by pouring the ferrocyanide solution into the acidified and boiling excess of the iron salt, the least quantity of alkali metal is retained, but even under these conditions the error would be 3½ per cent. too low in the case of the potassium compound, and if sufficient ammonia were present, as would probably be the case in the liquor prepared from spent oxide, the result would be 8 to 9 per cent. too low.

[1] *J. fur Gasbel.*, **43** [37], 696–97.

CHAPTER XVI

THE ESTIMATION AND SEPARATION OF THE IRON CYANOGEN COMPOUNDS, FERRICYANIDES, CARBONYLFERROYCYANIDES, AND NITROFERRICYANIDES

FERRICYANIDES may be readily detected in neutral or acid solutions by the addition of a solution of ferrous sulphate, which immediately forms a beautiful blue precipitate. The addition of a ferric salt solution, however, produces no precipitate, only a brownish coloration.

The determination of ferricyanides is easily accomplished by converting them into ferrocyanides by reduction, and then estimating the so formed ferrocyanides by any one of the methods described in the previous chapter that may be found most convenient.

This reduction of the ferricyanide is best performed by means of certain metallic hydroxides such as ferrous, manganous or cobaltous hydroxides in alkaline solutions. The liquid is first made alkaline with caustic soda or potash, an excess of the freshly precipitated metallic hydroxide added, the mixture warmed and the precipitate filtered off and thoroughly washed. This reaction may be expressed: With ferrous hydroxide:

$$2K_3Fe'''(CN)_6 + 2Fe(OH)_2 + 2KOH = 2K_4Fe''(CN)_6 + Fe_2(OH)_6.$$

With manganous hydroxide:

$$2K_3Fe'''(CN)_6 + 3Mn(OH)_2 + 2KOH = 2K_4Fe''(CN)_6 + M_3O_4 + 4H_2O.$$

And with cobaltous hydroxide :

$$2K_3Fe'''(CN)_6 + 3Co(OH)_2 + 2KOH = 2K_4Fe''(CN)_6 + Co_3O_4 + 4H_2O.$$

The ferricyanide may be directly estimated without previous conversion into ferrocyanide by any of the processes described below :

1. A weighed quantity of the ferricyanide, or a measured volume of the solution after evaporation to dryness is ignited with concentrated sulphuric acid, and the ammonia formed determined by distilling the dissolved and diluted residue with an excess of caustic soda into standard sulphuric acid, or by estimating the amount of iron in the residue.

Each cubic centimetre of N/10 sulphuric acid consumed in the former method will be equivalent to 0.005488 grm. of potassium ferricyanide or 0.003533 grm. of ferricyanogen, $'''Fe(CN)_6$, and the weight of oxide obtained in the latter case must be multiplied by 4.123 for potassium ferricyanide or by 2.65 for ferricyanogen.

2. The method described in the previous chapter for the estimation of ferrocyanides by distilling about half a gramme with dilute sulphuric acid and a little cuprous chloride, and estimating the cyanide formed by conducting the evolved hydrocyanic acid into caustic soda or potash solution, may be applied with equal ease and accuracy for the determination of ferricyanides if a somewhat larger quantity of cuprous chloride is added.

3. Ferricyanides may also be estimated by measuring the volume of nitrogen evolved on treating an alkaline solution with hydrazine sulphate. The reaction which takes place may be expressed by the equation :

$$4K_3Fe(CN)_6 + N_2H_4 + 4KOH = 4K_4Fe(CN)_6 + N_2 + 4H_2O.$$

The estimation may be carried out by introducing an excess of solid hydrazine sulphate into a nitrometer tube from below, and then adding 0·3–0·5 grm.

of the ferricyanide through the funnel followed by the alkali, and the evolved nitrogen measured.[1]

4. That hydrogen peroxide in presence of caustic alkalis will reduce ferricyanides to ferrocyanides quantitatively has been shown by J. Quincke, and also that the ferricyanide may be estimated by the amount of oxygen evolved.[2] The reaction may be expressed :

$$2K_3Fe(CN)_6 + 2KOH + H_2O_2 = 2K_4Fe(CN)_6 + 2H_2O + O_2.$$

From 5 to 10 c.c. of the ferricyanide solution is introduced into the closed end of a nitrometer tube with mercury, together with an equal volume of sodium hydroxide and followed by a solution of hydrogen peroxide ; the tube is then well shaken and the volume of gas measured. One cubic centimetre of oxygen at 0° C. and 760 mm. pressure is equivalent to 0.02945 $K_3Fe(CN)_6$ or 0.0279 at ordinary temperature and pressure.

The determination of the ferrocyanide formed by the above reaction, after boiling off the excess of hydrogen peroxide, has been suggested by G. Kassner.[3]

5. Determination by means of potassium iodide. This process[4] is based on the fact that iodine is liberated when potassium iodide is added to a dilute solution of a ferricyanide, which has been slightly acidified with hydrochloric acid :

$$2K_3Fe'''(CN)_6 + 2KI = 2K_4Fe''(CN)_6 + I_2.$$

The presence of the ferrocyanide interferes with the course of the reaction and must therefore be removed as soon as it is formed. This is accomplished by the addition of a slight excess of pure zinc sulphate, and the liberated iodine is then determined in the usual manner.

[1] P. R. Rây and H. K. Sen, *Z. anorg. Chem.* (1912), **76**, 380–86.

[2] *Z. anal. Chem.*, xxxi. 1 ; *J.C.S.* (1892), pp. 527.

[3] Abst, *J.C.S.* (1890), 834.

[4] W. Meklenberg, *Z. anorg. Chem.*, **67**, 322–38.

To carry out the estimation, a solution of the ferricyanide containing about 0.5 grm. is diluted with distilled water to 500 to 750 c.c., then 10 to 15 c.c. of concentrated hydrochloric acid (sp. gr. 1.19), a solution of 1 to 2 grm. of potassium iodide and 10 c.c. of a strong solution of zinc sulphate added. It is an advantage to add also 10 to 15 c.c. of a saturated solution of potassium chloride to cause the precipitated zinc ferrocyanide to settle more readily and prevent it becoming too gelatinous. The mixture after being well shaken and allowed to stand three or four minutes, is titrated with standard N/10 sodium thiosulphate solution until nearly all the free iodine is removed, and after standing for another two or three minutes the titration is completed. One cubic centimetre of N/10 $Na_2S_2O_3 = 0.032921$ grm. $K_3Fe(CN)_6$.

If both ferro- and ferricyanide exist in the same solution, the ferricyanide may be estimated by the method described above, and the ferrocyanide by taking a fresh portion of the solution, diluting it to 600 to 700 c.c. to which is then added 10 to 15 c.c. of concentrated hydrochloric acid, 40 to 60 c.c. of strong sodium acetate solution followed by N/10 permanganate in slight excess. The excess of permanganate is then determined by first adding potassium iodide solution and then titrating the liberated iodine with N/10 sodium thiosulphate.

The ferricyanide in the presence of weak acetic acid and in the absence of zinc salts, does not liberate iodine from potassium iodide. The number of cubic centimetres of permanganate solution consumed by the solution multiplied by the factor 0.03683, will give the measure of the ferrocyanide present in terms of potassium ferrocyanide, $K_4Fe(CN)_6$.

A process has been worked out by the author for the estimation of ferricyanides, in which advantage is taken of the fact that cobaltous hydroxide is oxidized by ferricyanides in alkaline solutions, and that the resulting cobaltosocobaltic hydroxide evolves chlorine

when the filtered and washed precipitate is subsequently boiled with dilute hydrochloric acid.

About 0.5 grm. of the ferricyanide is dissolved in 100 c.c. of water and treated with an excess of cobaltous hydroxide made alkaline with caustic soda. The mixture is then warmed for a minute or so and the black mixed cobalt hydroxides filtered off and thoroughly washed, transferred to a flask and distilled with dilute hydrochloric acid. The chlorine which is evolved is passed through two absorption flasks containing potassium iodide solution. The liberated iodine is then titrated with N/10 sodium thiosulphate, using starch solution as indicator. One cubic centimetre of the thiosulphate solution is equivalent to 0.03292 grm. potassium ferricyanide.

The reactions involved in this method may be expressed thus :

1. $2K_3Fe(CN)_6 + 3Co(OH)_2 + 2KOH = 2K_4Fe(CN)_6 + Co_3O_4 + 4H_2O$.
2. $Co_3O_4 + 8HCl = 3CoCl_2 + 4H_2O + Cl_2$.
3. $Cl_2 + 2KI = 2KCl + I_2$.

This method is applicable in the presence of ferrocyanides and other cyanogen compounds, and in the absence of other oxidizers.

Separation and estimation of ferro- and ferricyanides. Although the addition of a solution of ferric chloride to a solution of a ferrocyanide produces a deep blue precipitate of prussian blue, and to a pure ferricyanide solution only a darkening of the liquid but no precipitate, these facts cannot be applied as a method for the separation of the two salts. For contrary to the statement made so frequently in text-books, separation cannot be effected by this means, a very considerable quantity of the ferricyanide being carried down as a green iron compound with the ferrocyanide.

In fact, if ferric chloride solution is added to a solution of the two salts containing a very considerable excess of ferricyanide, a very finely divided green precipitate is obtained of a ferric ferroferricyanide, of

which 75 per cent. of the total cyanogen will be combined as ferricyanogen and the ratio of $''''Fe(CN)_6$: $'''Fe(CN)_6$, is as 1 : 3.[1]

These two iron cyanogen compounds may, however, be separated from other salts and from each other by taking advantage of the different properties of their zinc salts.

The solution, which must contain not more than 1 grm. of the mixed iron cyanogen compounds, is acidified with dilute hydrochloric or sulphuric acid, and the two compounds separated from other salts by the addition of an excess of zinc sulphate solution, and the mixed precipitate filtered and thoroughly washed. The precipitate is then digested with an excess of sodium carbonate solution when the whole of the ferricyanide of zinc will be decomposed and sodium ferricyanide pass into solution, but the ferrocyanide of zinc will be unattacked. The mixture is then filtered and washed. The filtrate, which contains the whole of the ferricyanide, is estimated as cyanide by distilling with dilute sulphuric acid and cuprous chloride into caustic soda solution. The precipitate left on the paper of basic ferrocyanide and carbonate of zinc is then also put into the distilling flask, together with the paper, dilute sulphuric acid and cuprous chloride added and distilled into caustic alkali solution in the same manner. The dilute cyanide solution obtained in each case is estimated by titration with N/10 $AgNO_3$, using potassium iodide as indicator, 1 c.c. of the silver solution being equivalent to 0.01097 $K_3Fe(CN)_6$ or 0.012277 $K_4Fe(CN)_6$ or 0.0070633 $Fe(CN)_6$.

Ammonia solution may be substituted for the sodium carbonate in the above separation of the zinc salts, zinc ferricyanide being readily dissolved by ammonia while the ferrocyanide is insoluble, but this method offers no advantage, and the precipitate is difficult to filter.

In the absence of salts, other than the ferro- and ferricyanide, separation may be easily obtained by

[1] H. E. Williams, *P.C.S.*, **29**, 54.

shaking the solution, made alkaline with sodium carbonate, with an excess of freshly precipitated zinc carbonate. The whole of the ferrocyanide is precipitated while the ferricyanide remains in solution.

Separation of ferro- and ferricyanide from each other and from other salts may be accomplished by the method proposed by Browning and Palmer,[1] which depends upon the fact that whereas a cadmium salt will precipitate both of the iron cyanogen compounds in a neutral or acid solution, a solution of a thorium salt only precipitates the ferrocyanide.

The solution of the mixed iron cyanogen compounds is acidified with acetic or hydrochloric acid and precipitated with a slight excess of thorium nitrate, a little asbestos being added to the liquid and well shaken to assist filtration. When the thorium ferrocyanide is filtered and thoroughly washed, a slight excess of cadmium chloride is added to the filtrate, which is again filtered from the cadmium ferricyanide. If the filtrate contains thiocyanates they may be separated by the addition of sulphate of copper solution and sodium bisulphite, and the cuprous thiocyanate estimated in the usual manner.

The precipitates of thorium ferrocyanide and cadmium ferricyanide can be separately converted into the corresponding soluble compounds and estimated by any of the methods described.

In the absence of other oxidizable salts the two iron cyanogen compounds may be estimated in the presence of each other by a modification of the permanganate method.

Sufficient of the solution to contain about 1.0 grm. of the total iron cyanogen compounds is taken and diluted to 400 to 500 c.c. acidified with dilute sulphuric acid and standard decinormal permanganate solution then run slowly in, with continued stirring, until the liquid takes a decided yellowish-red colour. The amount of permanganate solution used multiplied by

[1] *Z. anorg. Chem.* (1907), **54**, 315–18.

0.03683 will represent the weight of ferrocyanide present calculated as the potassium salt, $K_4Fe(CN)_6$.

If now a further and equal quantity of the solution is taken and boiled a short time with a solution of caustic soda and ferrous sulphate, or as the author prefers, caustic soda and manganous or cobaltous chloride, taking care that the alkali is present in excess, all the ferricyanide present will be reduced to ferrocyanide. The solution is filtered from the metallic hydroxide, which is thoroughly washed, and diluted to 400 to 500 c.c. acidified with dilute sulphuric acid and titrated with the permanganate solution as in the previous estimation. The quantity of permanganate consumed in this last operation represents the total ferro- and ferricyanide together, from which must be subtracted the amount used in the first determination, and the result multiplied by 0.03292, will express the amount of ferricyanide present, calculated as the potassium salt, $K_3Fe(CN)_6$.

Estimation of Carbonylferrocyanide. These salts may be estimated by any of the methods common to the iron cyanogen compounds, that is, they may be determined either volumetrically, by precipitation with a standard solution of copper sulphate, or by igniting the dry salt with strong sulphuric acid and estimating the ammonia formed, or the liberated iron.

Volumetric estimation by Standard Sulphate of Copper Solution. The ordinary copper sulphate solution used in the estimation of ferrocyanides may be used, but it must, of course, be first standardized on a carbonylferrocyanide. The calcium potassium salt is the best for this purpose as it crystallizes better than any other soluble carbonylferrocyanides, and is therefore readily obtained in a pure state. The composition of the salt in the crystalline state being, $CaKFe(CN)_5CO.5H_2O$.

One gramme of the pure salt is boiled with an excess of potassium carbonate, filtered and washed to 100 c.c. ; 25 c.c. of this solution are taken and placed in a titrating beaker with 50 c.c. of water, just acidified

with dilute sulphuric acid and 25 c.c. of a saturated solution of potassium chloride added, and the copper solution run gradually in, agitating the liquor the while until all the carbonylferrocyanide is precipitated.

The end-point is detected by dipping into the liquid a strip of filter-paper, and just touching the clear liquid that sucks up the paper, with a glass rod which has been dipped into a dilute solution of ferric chloride. The formation of a violet coloration at the point of contact of the two liquids, indicates that carbonylferrocyanides are still in solution, and more copper solution must be added, until no coloration is produced on repeating the test. The number of cubic centimetres of the copper solution so required divided into 0.25, will give the value for each 1 c.c. of copper solution for carbonylferrocyanide in terms of the calcium potassium salt, $CaKFe(CN)_5CO5H_2O$.

The green precipitate of cupric carbonylferrocyanide contains a small proportion of combined potassium, though considerably less in proportion than the brown precipitate obtained under similar conditions in the titration of ferrocyanides, but the addition of potassium salts recommended above is, nevertheless, advisable to obtain concordant and accurate results, and also as in the case of the ferrocyanides, the carbonylferrocyanide should be on the potassium base for estimation.

If the carbonylferrocyanide exists in an insoluble form in combination with a heavy metal, it should be first decomposed with a solution of potassium hydroxide or carbonate and filtered.

Estimation by Conversion of the Cyanogen into Ammonia. To carry out this method 0.5 grm. of the salt is weighed out and put into a kjeldahr flask and treated with 20 c.c. of concentrated sulphuric acid and 5 grm. of potassium sulphate, and heated for about two hours, when the following reaction takes place :

$$2K_3Fe(CN)_5CO + 20H_2SO_4 = 3K_2SO_4 + Fe_2(SO_4)_3 + 5(NH_4)_2SO_4 + 8CO_2 + 9SO_2 + 4CO.$$

the whole of the nitrogen being converted into ammonium sulphate, when the action is complete the acid liquor is poured into about 100 c.c. of distilled water and the flask thoroughly washed out, the diluted solution is transferred to a distilling flask of about 300 to 350 c.c. capacity, neutralized with an excess of caustic soda solution, and the ammonia distilled off through a condenser into a known volume of standard sulphuric acid. When the distillation is complete, the acid in the absorption flask is titrated back with standard caustic potash solution, using methyl orange as indicator.

One cubic centimetre of N/10 sulphuric acid will be neutralized by the ammonia formed from 0.00428 grm. of carbonylferrocyanogen, $'''Fe(CN)_5CO$, or 0.007662 grm. of crystallized calcium potassium carbonylferrocyanide.

This method is only accurate in the complete absence of any other nitrogen compound.

The iron liberated by the above reaction may also be used as a means of estimating these salts, but other iron cyanogen compounds or iron salts must be absent.

Half a gramme of the carbonylferrocyanide is ignited in a platinum dish with an excess of concentrated sulphuric acid in a manner similar to the method above described, care being taken that no loss occurs by spitting during the effervescent action which first takes place. When the reaction is complete, the bulk of the excess sulphuric acid should be gently evaporated off under a hood in a good draught. The contents of the dish are then dissolved in water, to which a little hydrochloric acid is added, and the iron estimated by standard permanganate solution after reduction to the ferrous state by metallic zinc. One part of iron is equivalent to 3.834 parts of carbonylferrocyanogen or 6.861 parts of the crystallized calcium potassium salt.

If the carbonylferrocyanides occur associated with other iron cyanogen compounds or impurities, as would usually be the case, they may be readily

separated by the following method, in which advantage is taken of the solubility of lead carbonylferrocyanide in neutral or acid solutions.

To the neutral or slightly acid solution, lead nitrate or acetate is added in excess. By this means the ferrocyanide is precipitated as the insoluble lead salt, while the carbonylferrocyanide remains in solution. The precipitate is filtered and thoroughly washed, the excess lead removed from the filtrate by the addition of a solution of sodium or potassium sulphate, and the precipitated lead sulphate filtered and thoroughly washed. The carbonylferrocyanide in the filtrate and washings is then precipitated by the addition of an excess of a ferric salt solution, the violet ferric carbonylferrocyanide filtered through a large filter and thoroughly washed. The precipitate, together with the paper, is then transferred to the beaker in which it was precipitated, and decomposed with 100 c.c. of a 3 per cent. solution of potassium hydroxide, the mixture being well stirred with a glass rod. It is then again filtered and washed, and the filtrate estimated according to one or other of the methods described above.

In the unusual presence of ferricyanides or nitroferricyanides, the mixed solution of the cyanogen compounds must first be boiled with ferrous or cobaltous hydroxide in the presence of sodium or potassium hydroxide. The two iron cyanogen compounds will then be converted into ferrocyanide, which may be separated from the solution with lead acetate after the liquid has been acidified with acetic acid.

Should the solution be free from ferro- or ferricyanide or other cyanogen compounds, the treatment with lead acetate may be omitted, and the carbonylferrocyanide directly precipitated with ferric chloride.

Estimation of Nitroferricyanides. These salts are readily detected by the deep violet coloration which takes place in solution, by the addition of an alkaline

sulphide. The estimation of nitroferricyanides is but rarely required, and little attention has been paid to this subject.

If the salt occurs free from iron or iron cyanogen compounds, it can be estimated by a determination of the iron in the residue after ignition with strong sulphuric acid, as in the method described under ferrocyanides. Instead of igniting the compound with concentrated sulphuric acid, it may be decomposed by boiling with a solution of ammonium or potassium persulphate, the basic ferric sulphate which is formed, dissolved in hydrochloric acid and the iron in solution estimated. The weight of ferric oxide obtained multiplied by 2.705 will express the amount of the nitroferrocyanogen radicle $''[Fe(CN)_5NO]$, in the weight of material taken.

A volumetric process has been described,[1] which depends upon the fact that as cadmium nitroferricyanide is soluble in ammonia, the cadmium may be precipitated as sulphide by a standard solution of sodium sulphide, the nitroferricyanide in solution acting as indicator, developing the well-known violet-purple colour with the slightest excess of soluble sulphide.

A known volume of the solution is precipitated by an excess of cadmium nitrate solution, the precipitated cadmium nitroferricyanide filtered, washed, dissolved in ammonia, and titrated with standard sodium sulphide solution until the appearance of a permanent violet colour.

An estimation may also be made by adding a known excess of a cadmium salt to the nitroferricyanide solution, the precipitate being filtered off and washed, and the excess of cadmium determined in the filtrate with the standard sulphide solution, using nitroferricyanide as indicator.

Nitroferricyanides may also be estimated by boiling

[1] Fonzes-Diacon and Carquet, *Bull. Soc. Chim.* (1903), **29** [13], 636–38 ; *J.S.C.I.*, **22**, 883.

with caustic alkalis, when the following reaction takes place :

$$36Na_2Fe(CN)_5NO + 83NaOH = 30Na_4Fe(CN)_6 + 3Fe_2O_3 + 35NaNO_2 + 40H_2O + NH_3.$$

The ferrocyanide, which is formed quantitatively, may be estimated as such.

CHAPTER XVII

ANALYSIS OF THIOCYANATES, OXY-CYANOGEN COMPOUNDS, CYANOGEN HALOIDS, AND CYANAMIDE

Estimation of Thiocyanates. Thiocyanates may be detected in solution by the deep blood-red coloration formed when a solution of ferric chloride is added to an acidified solution of the thiocyanate. This coloration is unaltered by the addition of hydrochloric acid, but disappears on adding an excess of mercuric chloride solution. They may also be detected by adding a solution of cupric chloride or sulphate to a dilute solution of the thiocyanate and passing a rapid current of sulphur dioxide through the liquid. In the presence of thiocyanates a finely divided white precipitate of the cuprous salt is formed.

Small quantities of thiocyanates may be detected in the solid state by adding ammonium molybdate and hydrochloric acid, and exposing the mixture to the action of hydrogen sulphide gas, the molybdate is reduced and molybdenum thiocyanate is produced, with the formation of an intense red or purple colour.

The determination of thiocyanates is accomplished either by conversion into the silver or copper salts, and estimating the salt volumetrically or by weighing, or by oxidizing the sulphur of the thiocyanate radicle with an oxidizing agent such as permanganate, nitric acid or iodine, and estimating either the amount of oxidizing agent used or the proportion of sulphuric acid formed by the oxidation of the sulphur.

Estimation by Silver Nitrate Solution. This simple and convenient method which has been proposed by

Volhard, is based on the fact that the addition of a solution of a thiocyanate to a solution of silver nitrate acidified by nitric acid, and containing a few cubic centimetres of a 10 per cent. solution of pure iron alum, does not form the red colour of ferric thiocyanate until the whole of the silver is precipitated as silver thiocyanate.

A solution of the thiocyanate of about 0.5 per cent. strength is put into a burette of 50 c.c. capacity, and run into a 150 c.c. beaker containing 20 c.c. of N/10 silver nitrate solution, 5 c.c. of 10 per cent. of iron alum solution, 10 c.c. of strong pure nitric acid and 50 c.c. of distilled water, until a slight red coloration of ferric thiocyanate is produced, which is permanent on shaking.

The amount of thiocyanate precipitated by 20 c.c. of N/10 silver nitrate solution would be 0.162 grm. of sodium thiocyanate or 0.152 grm. for the ammonium salt, etc., and the number of cubic centimetres of thiocyanate solution required to precipitate the 20 c.c. of silver solution will contain this amount of thiocyanate, a simple proportion sum will then give the amount of thiocyanate in 100 c.c. of the solution.

For example, 0.5 grm. of pure dry ammonium thiocyanate were dissolved in distilled water, diluted to 100 c.c. and placed in a burette, and then run slowly into a beaker containing 20 c.c. of the silver solution and other ingredients as described above until the first appearance of a faint but permanent red colour. At this point 30.6 c.c. of the thiocyanate solution had been consumed. Now as 20 c.c. of the standard silver solution will exactly precipitate 0.1522 grm. of ammonium thiocyanate, it follows that this amount must have existed in the 30.6 c.c. of the solution used, and that therefore 100 c.c. must have contained 0.4974, the amount of real ammonium thiocyanate in the 0.5 grm. taken, which multiplied by 200 = 99.48 per cent.

For the determination of thiocyanates by this method, chlorides or any other acid radicle capable of

forming silver salts insoluble in cold dilute nitric acid, must of course be absent. In the event of their presence the thiocyanate should be separated as the cuprous salt in the manner described below, and then filtered and washed, the precipitate boiled with pure caustic potash solution filtered, the cuprous hydroxide thoroughly washed and the filtrate diluted to a definite volume and estimated in the manner described above.

Separation and Estimation as Cuprous Thiocyanate. A solution of a thiocyanate, which should not contain more than 1 grm. of the salt is acidified with hydrochloric or sulphuric acid, a solution of sodium bisulphite added, followed by the addition of an excess of cupric sulphate or chloride. The thiocyanate is then precipitated as the finely divided white cuprous salt, which should be left to stand for at least twenty-four hours. The precipitate may then be filtered on a tarred filter and thoroughly washed, and finally dried at 105° C. and weighed. The weight of cuprous thiocyanate obtained multiplied by 0.4775, will equal the weight of thiocyanogen ('CNS), or the cuprous thiocyanate may be removed from the paper, the paper burnt and the ash added to the bulk. The whole is then digested for some time with an excess of ammonium sulphide, and the residue of cuprous sulphide filtered, thoroughly washed and ignited at a gentle heat in a crucible with an excess of pure sulphur. The weight of cuprous sulphide obtained multiplied by 0.73 will equal the weight of thiocyanogen ('CNS).

A simpler and quicker method is to decompose the washed thiocyanate with pure caustic potash, filter and wash to a definite volume, and estimate the solution with silver nitrate as described above.

In the precipitation of the cuprous thiocyanate, ferrous sulphate or sulphur dioxide gas may be substituted, the latter with advantage, for the sodium bisulphite, but the gas should be bubbled through until the solution smells strongly of the gas.

Ferrocyanides, if also present, may be removed by

a first precipitation with ferric or zinc salts, and the thiocyanates precipitated from the filtrate after the ferrocyanides has been filtered off and thoroughly washed. Chlorides or bromides do not interfere, but iodides should be absent, otherwise the precipitate will be contaminated with cuprous iodide, which would not only give too high a reading when the cuprous salt was weighed as thiocyanate or sulphide, but would also be returned as thiocyanate if the determination were made by means of silver nitrate.

This method of precipitating the cuprous thiocyanate may be applied as a means of estimating the thiocyanates volumetrically.

A standard solution of sulphate of copper is run gradually into the thiocyanate solution, which is kept warm, and to which an excess of sodium bisulphite has been added. After each addition of the copper solution, the white precipitate of cuprous thiocyanate is allowed to settle, and a drop of the clear liquid tested with a drop of potassium ferrocyanide on a white tile. The appearance of a brown coloration immediately the two liquids meet indicates the presence of an excess of copper, and the complete precipitation of all the thiocyanate. A convenient strength of the solution is the decinormal—24.97 gr. $CuSO_45H_2O$ to 1000 c.c.—1 c.c. of this solution will exactly precipitate 0.0058 grm. thiocyanogen ('CNS) or 0.00761 grm. of ammonium thiocyanate, etc.

Estimation by Oxidation with Potassium Permanganate. The addition of a solution of potassium permanganate to an acidified solution of a thiocyanate results in the oxidation of the sulphur of the thiocyanate to sulphuric acid, and the liberation of hydrocyanic acid :

$$5KCNS + 12H_2SO_4 + 6KMnO_4 = 11KHSO_4 + 6MnSO_4 + 5HCN + 4H_2O.$$

A solution of the thiocyanate, which should not contain more than 0.1 to 0.05 calculated as the potassium salt, is considerably diluted, and if the solution is

alkaline it should be neutralized with dilute sulphuric acid, and 50 c.c. of 10 per cent. acid added in excess. Decinormal permanganate solution is then run into the thiocyanate solution slowly with constant stirring until the first appearance of a faint red tinge, permanent on agitation, due to an excess of permanganate solution.

Each cubic centimetre of decinormal permanganate solution consumed is equivalent to 0.001619 grm. KCNS, or 0.000968 'CNS.

The researches of H. Grossmann and L. Hölter [1] tend to show that the oxidation of thiocyanates by permanganate is incomplete, and that only about 95 per cent. of the thiocyanate is oxidized. It would appear under these circumstances that the permanganate solution should be standardized against pure thiocyanate, and subsequent estimations made under identical conditions.

This method is only applicable to comparatively pure solutions, and no oxidizable body other than the thiocyanate must of course be present. The thiocyanate may be separated from impurities by precipitation as the cuprous salt in the manner previously described, and converted into the pure solution by treatment with caustic potash, or the cuprous salt may be dissolved in ammonia diluted with water, then acidified with dilute sulphuric acid, and while still warm titrated with the permanganate solution.[2]

The time occupied by the addition of the permanganate solution is considered by K. Schroder [3] an important factor of this method, and one which is liable to give low readings, due to the formation of complex compounds not taken into consideration in the simple reaction expressed above ; and he proposes the following modification. A measured excess of standard permanganate solution is placed in a flask and acidified with 10 c.c. of dilute sulphuric acid

[1] *Chem. Z.*, **33**, 348.

[2] Leon Roumet, *Ann. Chem. anal.* (1911), **16**, 336–37.

[3] *Z. offentl. Chem.*, **15**, 321–36.

(1 to 1) and 5 c.c. of phosphoric acid (sp. gr. 1.7), the thiocyanate solution being then added, followed immediately by a measured and excessive quantity of hydrogen peroxide which has previously been standardized against the permanganate solution. The hydrogen peroxide in excess is then determined by the permanganate.

From the total number of cubic centimetres of permanganate solution used, deduct the permanganate equivalent of the hydrogen peroxide, the remainder will represent the number of cubic centimetres of permanganate consumed by the thiocyanate, which must be multiplied by 0.001619 to obtain the amount of thiocyanate expressed as potassium thiocyanate.

Instead of hydrogen peroxide, standard oxalic acid may be used for titrating the excess of permanganate.

Oxidation of the Thiocyanate and Estimation as Barium Sulphate. In the absence of other sulphur compounds, thiocyanates may be readily estimated by this method. A weighed quantity of the thiocyanate or a measured quantity of the solution containing about 0.5 grm. is carefully added to about 100 c.c. of dilute nitric acid, boiling in a 250 c.c. beaker. An immediate and sometimes somewhat violent oxidation takes place. After the action has subsided, the liquor is boiled for from five to ten minutes, and the sulphuric acid produced by the oxidation of the sulphur of the thiocyanate is precipitated with a solution of barium chloride or nitrate, and the resulting barium sulphate filtered and estimated in the usual manner, 233.44 parts of barium sulphate are produced for each 58.08 parts of thiocyanogen ('CNS), and if the weight of barium sulphate is multiplied by the factor 0.2488, the result will express the amount of thiocyanogen ('CNS) in the material taken.

Potassium permanganate, bromine and certain other oxidizing agents, if free from sulphur compounds, may be substituted for the nitric acid.

Estimation by Oxidation with Standard Iodine Solution. To a dilute but measured volume of a solution of a thiocyanate, 2 grm. of sodium bicarbonate are added, followed by 50 c.c. of N/5 iodine solution, and the whole allowed to stand in a stoppered vessel for about four hours; hydrochloric acid is then added, and the iodine in excess titrated with N/10 sodium thiosulphate solution. The end-point is observed by the complete disappearance of the yellow colour of the iodine as starch paste cannot be used.

Another convenient volumetric method has been suggested by W. König,[1] which depends on the reaction of bromine with thiocyanates whereby sulphuric and hydrobromic acids are produced quantitatively, thus:

$$2KCNS + 8Br_2 + 8H_2O = K_2SO_4 + H_2SO_4 + 2BrCN + 14HBr.$$

The thiocyanate solution is treated with the bromine and the solution is then titrated with standard alkali.

W. Feld[2] has proposed a method based on the reduction of thiocyanates in solution by nascent hydrogen produced by the action of hydrochloric acid on metallic aluminium:

$$3KCNS + 4Al + 18HCl = 3KCl + 4AlCl_3 + 3NH_4Cl + 3C + 3H_2S.$$

The hydrogen sulphide evolved may be estimated by absorbing it in a known excess of standard iodine solution, and the excess iodine then estimated by titration with decinormal sodium thiosulphate solution; or the ammonia may be estimated by distilling the solution after the addition of an excess of sodium or potassium hydroxide, into standard acid.

Insoluble thiocyanates are estimated by first converting them into a soluble salt, by digesting them with an excess of ammonium sulphide. The mixture is then filtered, the insoluble sulphide thoroughly washed, and the filtrate evaporated to dryness on the water-bath to remove the excess of ammonium sulphide,

[1] *J. pr. Chem.* (1911), ii. **84**, 558–60.
[2] *J. Gasbeleuch* (1903), **46**, 561.

and the residue treated with water to dissolve the ammonium thiocyanate, which may be estimated by any of the methods described above.

If free from other sulphur compounds, they may also be estimated by fusion with a mixture of sodium carbonate and potassium nitrate, and estimating the sulphate formed, by dissolving the fused mass in water, neutralizing with hydrochloric acid and precipitating with barium chloride.

Any base combined with the soluble thiocyanate may be estimated by evaporating the solution to dryness with an excess of sulphuric acid, by which means the thiocyanate is destroyed and the metal left as the sulphate. Ammonium can, of course, be estimated in the usual manner by distilling the liquor with dilute caustic alkali, into standard acid.

Very small amounts of thiocyanate may be estimated by comparing the colour produced by the addition of ferric chloride with that of an equal volume of solution containing a known quantity of thiocyanate and treated in the same way. It is necessary that equal volumes of ferric chloride should be added both to the solution to be tested and the standard, for it has been shown that a soluble thiocyanate is not completely converted into ferric thiocyanate by the addition of the equivalent quantity of ferric salt, but that the reaction only approaches completion when a very large excess of ferric salt is present. The results obtained by this method are only approximately correct.

Very small quantities of thiocyanates, such as that existing in human saliva, may be detected by treating 12 to 15 c.c. of the liquid, or a small quantity of the powdered material if the substance is a solid, with 40 c.c. of absolute alcohol, and filtering. The filtrate is then concentrated to about 6 to 7 c.c. and again filtered. If now mercurous chloride is added to the concentrated filtrate, the salt will be reduced in the cold to metallic mercury, a reaction which is characteristic of thiocyanates.[1]

[1] E. Pallacci, *Chem. Zentr.* (1908), 1, 1576.

DETERMINATION OF CYANATES

Cyanates are readily detected by the intense blue colour of the double potassium cobalt cyanate, which is precipitated in small deep blue quadratic crystals when a cobalt salt is added to a solution of a potassium or other cyanate in the presence of a potassium salt, acidified with acetic acid.

If cyanates are tested for in the presence of cyanides, all the cyanide must first be decomposed by passing excess of carbon dioxide through the solution, and removing the excess of potassium carbonate by the addition of 95 per cent. alcohol and applying the test to the filtrate.

The general method for the estimation of a cyanate is that proposed by Herting,[1] which depends on the decomposition which these salts undergo in acid solution, whereby the liberated cyanic acid is decomposed into carbon dioxide and ammonia, the latter immediately combining with the acid to form the corresponding ammonium salt:

$$KCNO + 2HCl + H_2O = KCl + NH_4Cl + CO_2.$$

About 0.2 to 0.5 grm. of the cyanate or a measured quantity of material, or solution supposed to contain this amount, is dissolved in a little water, dilute hydrochloric or sulphuric acid added, and the solution boiled for some time. The solution is then transferred to a distilling flask, neutralized with an excess of caustic potash or soda and distilled into a measured quantity of standard sulphuric acid. The amount of acid neutralized by the ammonia is determined by titrating the excess standard acid with standard alkali, using methyl orange as indicator.

Cyanides do not interfere with this test, the hydrocyanic acid liberated by the mineral acid being driven off in the subsequent boiling. Ferrocyanides, ferricyanides, carbonylferrocyanides and nitroferricyanides

[1] *Z. angew. Chem.* (1901), **24**, 585.

if present, may be first precipitated, after acidification, by the addition of ferric or ferrous salts, according to the particular iron cyanogen compound present, but the precipitate so obtained, must be added to the alkaline solution in the still when the ammonia is to be determined, for it is impossible to precipitate ferrocyanides, etc., in the presence of ammonium salts without some of the ammonium being combined in the precipitated compound.

Milbauer has suggested the use of potassium hydrogen sulphate in place of the free mineral acid used above.[1]

Estimation by means of the Silver Salt. The cyanate may be precipitated as the silver salt by the addition of a solution of silver nitrate, and the white silver cyanate filtered off, thoroughly washed and digested in a known volume of standard nitric acid for about one hour on the water-bath. By this treatment the cyanate is decomposed thus :

$$H_2O + AgCNO + 2HNO_3 = AgNO_3 + NH_4NO_3 + CO_2.$$

The amount of cyanate may be determined by :

1. Estimating the excess nitric acid by titration with standard alkali solution.

2. Estimation of the ammonia by distilling with an excess of alkali into standard acid.

3. By titrating the silver nitrate formed by means of standard ammonium thiocyanate, using iron alum as indicator or by titrating with N/10 sodium chloride, after neutralizing the liquor, using potassium chromate as indicator.

Each cubic centimetre of normal nitric acid consumed will be equivalent to 0.0406 grm. of potassium cyanate, and each cubic centimetre of N/10 ammonium thiocyanate or sodium chloride will be equivalent to 0.00811 grm. KCNO.

Chlorides, bromides, iodides, cyanides, or ferrocyanides do not interfere with this test ; they will, of course, be precipitated along with the silver cyanate,

[1] *Z. anal. Chem.* (1903), **42**, 77.

but they do not decompose when treated with warm dilute nitric acid. If, however, cyanide of silver occurs in the precipitate, soluble chlorides must be entirely absent from the nitric acid solution.

DETECTION OF CYANURIC ACID

If the acid exists in the solid state, it is introduced into a short narrow tube after thorough drying, and gently heated. The presence of cyanuric acid can be readily detected by the very characteristic smell of cyanic acid, 1 molecule of cyanuric acid decomposing on heating into 3 molecules of cyanic acid :

$$H_3C_3N_3O_3 = 3HCNO.$$

If the acid is in solution a small quantity is warmed on a watch-glass with a few cubic centimetres of very strong caustic soda solution for a moment over a pointed flame, trisodic cyanurate crystallizes out in delicate needles radiating outwards from the point of heating, but redissolve on cooling if the solution is not too strong,[1] the salt being much less soluble in boiling solutions than in cold.

The addition of a drop of an ammoniacal solution of copper sulphate to a solution of the acid in dilute ammonia yields a beautiful pink copper salt.

ESTIMATION OF MERCURY FULMINATE AND THE FULMINATES

Mercury fulminate as used in cap composition is generally mixed with other bodies, such as antimony sulphide, sulphur, potassium chlorate or nitrate, or meal powder. The general method for the estimation of the fulminate is a volumetric one described by Brownsdon,[2] which is based on the reaction of mercury fulminate with a solution of sodium thiosulphate whereby alkali is liberated, which may be accurately

[1] Hofmann, *Ber.*, **3**, 770.

[2] *Chem. News* (1904), **89**, 303 ; *J.S.C.I.* (1905), **24**, 381.

titrated with standard acid, the amount of alkali liberated being proportional to the fulminate.

It is usual to standardize the method on pure mercury fulminate prepared as described below. A good sample of commercial fulminate is dissolved in dilute potassium cyanide solution, filtered from any insoluble matter that may be present, and the fulminate reprecipitated by the addition of dilute nitric acid; the precipitate is filtered off, thoroughly washed, and dried very carefully at 80° C. Of the so purified compound weigh out 0.05 grm. dissolve in about 30 c.c. of water, and then add 1 grm. of pure sodium thiosulphate. The mixture is then thoroughly shaken and diluted to 100 c.c., 25 c.c. of this solution are taken and titrated with standard acid, using methyl orange as indicator. This titration should be repeated and the mean of the figures taken to obtain the amount of mercury fulminate equivalent to 1 c.c. of standard acid.

The analysis of the commercial salt is carried out in an almost identical manner to the standard test just described for the pure salt. Not more than 0.05 grm. of the fulminate should be taken, and the solution after treatment with the sodium thiosulphate must be filtered from any antimony sulphide or other insoluble matter that may be present. The filtrate must be diluted to 100 c.c., and 25 c.c. taken for the estimation.

The fulminate may also be estimated by determining the carbon and nitrogen by combustion if a very large quantity of cupric oxide is used, but it would, of course, be necessary to remove the mercury before absorbing the products of combustion. This may be easily done by passing the combustion gases first through a tube containing gold leaf.

The mercury may be estimated by dissolving a weighed quantity of the sample in ammonia or potassium cyanide solution, and precipitating the mercury in the filtered liquor by ammonium sulphide.

Any soluble salts, such as potassium chlorate or nitrate may be separated by first washing with water.

Mercurous compounds may be detected by treatment with hydrochloric acid in which the fulminate is readily soluble, but the mercurous chloride formed by the action of the acid on the mercurous compounds remains unattacked or dissolves only with difficulty.

The presence of oxalate is detected and estimated by dissolving a weighed quantity of the material in ammonia solution, and filtered from any insoluble matter that may be present. To the filtrate sufficient ammonium sulphide is added to precipitate all the mercury as sulphide. The black precipitated sulphide is filtered and washed, and to the filtrate is added calcium chloride, together with more ammonia if required, to precipitate the oxalate as the calcium salt, which may be filtered off and estimated by any of the well-known methods.

The preparation of the crystalline pyridine compound for the purification of mercury fulminate is recommended by Andreas Salonina,[1] the compound being subsequently decomposed by water. He also recommends the estimation of the mercury by electrolysis.

ANALYSIS OF CALCIUM CYANAMIDE

Commercial calcium cyanamide (nitrolime) when freshly prepared contains its nitrogen principally in the form of calcium cyanamide, but after storing for some time certain changes take place due principally to the carbon dioxide and moisture in the air. The product then contains besides the unaltered calcium cyanamide, some calcium hydroxide and carbonate, dicyandiamine, urea, and possibly other nitrogen compounds.

For the estimation of the various nitrogen compounds N. Caro and others have worked out the following method which depends principally on the fact that cyanamide is precipitated by a salt of silver in the presence of an excess of ammonia while the

[1] *Zeitsch. Schiess Sprengstoffwesen* (1910), **5**, 41–6

silver dicyandiamide is soluble, but the latter may be precipitated in the filtrate by the addition of a solution of potassium hydroxide.

Ten grammes of the crude calcium cyanamide are placed in a 500 c.c. stoppered flask and treated with 400 to 450 c.c. of distilled water and agitated in a machine for two and a half hours. The mixture is then made up to 500 c.c. and filtered through a dry filter: 250 c.c. of the filtrate are treated with an ammoniacal solution of silver nitrate (prepared by adding 400 c.c. of a 10 per cent. solution of ammonia to a solution of 100 grm. silver nitrate, and diluting the mixture to 1000 c.c.) and diluted to 400 c.c. The precipitate of silver cyanamide is then carefully filtered through a dry filter and washed, but the wash water must be kept separate. When the precipitate is thoroughly washed the nitrogen is determined by Kjeldahl's method.

The dicyandiamide is determined by taking 300 c.c. of the undiluted filtrate from the silver cyanamide, adding an excess of potassium hydroxide solution, and diluting the mixture to 400 c.c. and boiling. The precipitated silver dicyandiamide is filtered through a dry filter and washed, but keeping the wash water separate and the nitrogen in the precipitate determined as before.

Of the undiluted filtrate in which any urea existing in the original calcium cyanamide will be dissolved, take 300 c.c. and evaporate down, and precipitate all excess of silver by passing hydrogen sulphide through the liquor, the excess of the latter gas is expelled by passing a rapid current of carbon dioxide through the solution. The solution is then diluted to 400 c.c. and the nitrogen determined in 100 c.c. after evaporating to dryness, and the result calculated as urea.[1] Small quantities of urea are said to be always present in commercial cyanamide.[2]

The dicyandiamide may be directly determined without first separating the cyanamide, by shaking

[1] *Z. angew Chem.* (1910), **23**, 2405–17.

[2] Ulpiani and Caro, *J.S.C.I.*, **30**, 23.

10 grm. of the calcium cyanamide for about one hour with 250 c.c. of 94 per cent. alcohol and then filtering; 100 c.c. of the filtrate are evaporated to dryness treated with hot water, followed by 10 c.c. of silver acetate solution and then filtered, and the precipitate washed. The filtrate is then mixed with 10 c.c. of a 10 per cent. solution of potassium hydroxide, and at once filtered, and the nitrogen in the precipitate determined by Kjeldahl's method.[1]

As the addition of alkalis and certain salts in small quantities to the calcium carbide before treatment with the nitrogen is liable to give rise to traces of cyanide in the resulting calcium cyanamide, these compounds should be tested for, and estimated if found to be present.

A direct estimation of the cyanide by Liebig's method on the aqueous extract of the calcium cyanamide cannot be accurately made, as the cyanamide and dicyandiamide which would also be in solution, would mask the end reaction. Feld's method, however, yields satisfactory and accurate results.[2]

One or two grammes of the substance are boiled in a distilling flask with an excess of a solution of lead nitrate and the distillate absorbed in a solution of potassium or sodium hydroxide. The dilute cyanide solution so obtained is then titrated with decinormal silver nitrate solution in the usual manner, after the addition of a few drops of potassium iodide solution.[3]

Monnier proposed for the estimation of cyanamide, to precipitate the compound from its solutions in the usual manner by the addition of aqueous ammonia and silver nitrate solution, then filter and wash the precipitate, and dissolve in dilute nitric acid, and titrate the silver with standard potassium thiocyanate solution, using iron alum as indicator. This method, however, has been shown to be unreliable[4] as basic

[1] A. Stuntzer and Söll, *Z. angew. Chem.* (1910), **23**, 1873–74; *J.C.S.* (1910), ii. 1009.

[2] *J.S.C.I.* (1903), 1065. [3] *J.S.C.I.*, **30**, 23, N. Caro.

[4] A. Stutzer, *Chem. Zeit.*, **35**, 694.

compounds are formed containing more or less silver than that necessary for pure silver cyanamide. Caro's method of determining the nitrogen in the precipitate as described above is, however, quite accurate.

The total nitrogen may be determined, either by Kjeldahl's method or by that of Förster. In the former method 0.5 grm. of the substance is heated with 30 grm. of concentrated sulphuric acid and 1 grm. of anhydrous copper sulphate ; the addition of potassium sulphate, phosphorus pentoxide or mercury offer no advantage.[1] In the latter method half a gramme of the substance is heated with sulphuric acid, to which is added salicylic acid and sodium thiosulphate or zinc dust.

DETERMINATION OF CYANOGEN HALOIDS

Cyanogen bromide may be determined by a method based on the reaction of the compound in aqueous solutions with hydrochloric acid, when hydrocyanic acid, free chlorine and bromine are formed :

$$2BrCN + 2HCl = 2HCN + Br_2 + Cl_2.$$

A few drops of strong hydrochloric acid are added to the aqueous solution of cyanogen bromide, followed by an excess of a solution of potassium iodide, iodine is liberated in quantities equivalent to the free chlorine and bromine :

$$B_2 + Cl_2 + 4KI = 2KBr + 2KCl + 2I_2.$$

The free iodine in solution is then estimated in the usual manner by titration with a standard solution of sodium thiosulphate, using starch paste as indicator.

Cyanogen chloride may also be estimated in a similar manner :

$$CNCl + HCl + 2KI = 2KCl + I_2 + HCN.$$

Cyanogen iodide, although quite stable towards oxidizing agents, is very readily decomposed by such

[1] R. Monnier, *Chem. Zeit.* (1911), **35**, 601 ; *J.C.S.* (1911), ii 668.

reducing agents as hydriodic acid, hydrogen sulphide or sulphurous acid, and may be determined volumetrically by hydriodic acid or sulphurous acid. It has sometimes been detected in commercial iodine,[1] in which it may be detected by adding a solution of sodium thiosulphate to the iodine solution after acidification with a drop of hydrochloric acid, until nearly all the iodine has reacted, and then adding to the resulting solution ferrous sulphate and an alkali. On acidification a precipitate of prussian blue will result if cyanogen be present with the iodine.

[1] Meincke, *J.C.S.* (1893), ii. 246.

TABLE I

INTERNATIONAL ATOMIC WEIGHTS

O = 16

Aluminium	=	Al	27.1	Iridium	=	Ir	193.1
Antimony	=	Sb	120.2	Iron	=	Fe	55.84
Argon	=	A	39.88	Krypton	=	Kr	82.92
Arsenic	=	As	74.96	Lanthanum	=	La	139.0
Barium	=	Ba	137.37	Lead	=	Pb	207.10
Bismuth	=	Bi	208.0	Lithium	=	Li	6.94
Boron	=	B	11.0	Lutecium	=	Lu	174.0
Bromine	=	Br	79.92	Magnesium	=	Mg	24.32
Cadmium	=	Cd	112.40	Manganese	=	Mn	54.93
Caesium	=	Cs	132.81	Mercury	=	Hg	200.60
Calcium	=	Ca	40.07	Molybdenum	=	Mo	96.0
Carbon	=	C	12.00	Neodymium	=	Nd	144.3
Cerium	=	Ce	140.25	Neon	=	Ne	20.2
Chlorine	=	Cl	35.46	Nickel	=	Ni	58.68
Chromium	=	Cr	52.0	Niton (radium emanation)	=	Nt	222.4
Cobalt	=	Co	58.97	Nitrogen	=	N	14.01
Columbium	=	Cb	93.50	Osmium	=	Os	190.9
Copper	=	Cu	63.57	Oxygen	=	O	16.00
Dysprosium	=	Dy	162.50	Palladium	=	Pd	106.70
Erbium	=	Er	167.70	Phosphorus	=	P	31.04
Europium	=	En	152.0	Platinum	=	Pt	195.20
Fluorine	=	F	19.0	Potassium	=	K	39.10
Gadolinium	=	Gd	157.3	Praseodymium	=	Pr	140.60
Gallium	=	Ga	69.9	Radium	=	Ra	226.4
Germanium	=	Ge	72.5	Rhodium	=	Rh	102.9
Glucinium	=	Gl	9.1	Rubidium	=	Rb	85.45
Gold	=	Au	197.2	Ruthenium	=	Ru	101.7
Helium	=	He	3.99	Samarium	=	Sa	150.4
Holmium	=	Ho	163.5	Scandium	=	Sc	44.1
Hydrogen	=	H	1.008	Selenium	=	Se	79.2
Indium	=	In	114.8				
Iodine	=	I	126.92				

Silicon	=	Si	28.3	Titanium	=	Ti	48.1
Silver	=	Ag	107.88	Tungsten	=	W	184.0
Sodium	=	Na	23.00	Uranium	=	U	238.5
Strontium	=	Sr	87.63	Vanadium	=	V	51.0
Sulphur	=	S	32.07	Xenon	=	Xe	130.2
Tantalum	=	Ta	181.50	Ytterbium (Neoytterbium)	=	Yb	172.0
Tellurium	=	Te	127.50	Yttrium	=	Yt	89.0
Terbium	=	Tb	159.20	Zinc	=	Zn	65.37
Thallium	=	Tl	204.0	Zirconium	=	Zr	90.6
Thorium	=	Th	232.4				
Thulium	=	Tm	168.5				
Tin	=	Sn	119.0				

TABLE II

N/10 PERMANGANATE OF POTASSIUM SOLUTION

3.1606 grammes of pure potassium permanganate dissolved in 1000 c.c. of water at 15.5° C.

1 c.c. of the standard solution is equivalent to—

0.02119	$Fe''(CN)_6$
0.02119	$Fe'''(CN)_6$
0.03683	$K_4Fe(CN)_6$
0.042235	$K_4Fe(CN)_63H_2O$
0.03039	$Na_4Fe(CN)_6$
0.048406	$Na_4Fe(CN)_610H_2O$
0.028635	$Fe_4[Fe(CN)_6]_3$
0.03292	$K_3Fe(CN)_6$
0.02809	$Na_3Fe(CN)_6$
0.031693	$Na_3Fe(CN)_62H_2O$
0.000968	'(CNS)
0.0013513	NaCNS
0.0016197	KCNS
0.0012687	NH_4CNS
0.0020275	CuCNS
0.031428	$Na_2Fe(CN)_5NO$
0.0357518	$Na_2Fe(CN)_5NO2H_2O$

The above solution should be standardized against standard N/10 oxalic acid solution, or a solution of freshly prepared and pure ferrous ammonium sulphate or pure iron wire in hydrochloric acid.

It may also be standardized for the purpose of ferrocyanide estimation against pure dry calcium potassium ferrocyanide ; this salt is easily prepared in a state of great purity and is anhydrous.

One gramme of calcium potassium ferrocyanide should require 30.3 c.c. of N/10 permanganate solution.

TABLE III

STANDARD N/10 SILVER NITRATE SOLUTION

16.989 grm. of pure silver nitrate dissolved in 1000 c.c. of water at 15.5° C.

One c.c. of standard solution is equivalent to—	
0.005202	$(CN)'$
0.005403	HCN
0.013022	KCN
0.009802	NaCN
0.025262	$Hg(CN)_2$
0.009209	$Ca(CN)_2$
0.0070633	$Fe'''(CN)_6$ or $Fe''(CN)_6$
0.012277	$K_4Fe(CN)_6$
0.014078	$K_4Fe(CN)_63H_2O$
0.010130	$Na_4Fe(CN)_6$
0.016135	$Na_4Fe(CN)_610H_2O$
0.009545	$Fe_4[Fe(CN)_6]_3$
0.003546	Cl
0.005846	NaCl
0.007456	KCl
0.010973	$K_3Fe(CN)_6$
0.009363	$Na_3Fe(CN)_6$
0.005808	'CNS
0.009718	KCNS
0.008108	NaCNS
0.007612	NH_4CNS
0.0078115	$Ca(CNS)_2$
0.012165	CuCNS
0.010476	$Na_2Fe(CN)_5NO$
0.0119172	$Na_2Fe(CN)_5NO2H_2O$

The above solution should be standardized against a N/10 solution of sodium chloride containing 5.846 gr. per 1000 c.c. at 15.5° C. Each 50 c.c. of this solution should be precipitated exactly by 50 c.c. of N/10 silver solution, using a few drops of potassium chromate as indicator.

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